

Rovibrational quenching calculations of C_2^- in collision with H_2

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The molecular anion C_2^- has been of interest in the past few years as a candidate for laser cooling due to its electronic structure and favorable branching ratios to the ground electronic and vibrational states. Molecular hydrogen has been used by the Wester group at Innsbruck as a buffer gas to cool the molecule's internal rovibrational motion. In the present work we generate a five-dimensional (5D) interaction potential for the system by considering the H_2 as a rigid rotor and the C_2^- as a rotating-vibrating diatomic molecule. We then calculate the cross sections and rate coefficients for rovibrational inelastic collisions of C_2^- with both para- and ortho- H_2 on this 5D *ab initio* potential energy surface using quantum scattering theory for the dynamics. The rates for vibrational quenching are obtained over a range of temperatures that covers the single point measured by the experiments. A comparison is also made with earlier results which had used a simpler 3D interaction potential. Para- H_2 is found to be more efficient than ortho- H_2 (with or without also undergoing rotational excitation) in cooling C_2^- . The rate coefficients for cooling the anions have been computed by appropriately weighting the ortho- and para- H_2 and compared with the available experimental result at 20 K. The computed results are nearly two orders of magnitude larger than the single experimental point. When the vibrational deexcitation rate coefficients are employed without any concurrent rotational excitations in the final C_2^- anions (a situation considered to be nonphysical under the present experimental setup), the properly averaged results are found to get smaller and to become very close to the existing experimental measurements. The robustness of the present results is tested and confirmed. The implications of these results for laser cooling of C_2^- are analyzed and discussed.

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I. INTRODUCTION

Laser cooling of molecules is currently an active area of research [1] since, with the direct preparation of ultracold molecular ensembles in magneto-optical traps [2], numerous experiments on molecular quantum control, precision

spectroscopy [3], and ultracold chemistry [4] have become accessible. For atoms, laser cooling of neutral and charged species has been a workhorse for many years, while for molecules no charged molecular species has yet been successfully laser cooled. The main reason for it is that, as it happens, molecular ions with bound excited electronic states below the first fragmentation threshold which can be excited with suitable narrowband lasers are hard to come by. Furthermore, a near optimal Franck-Condon overlap of the vibrational wave functions of the ground and excited electronic states is required to make the closed optical cycles feasible.

As a matter of fact, the diatomic carbon molecular anion has been identified as an interesting exception [5], as it possesses several bound excited electronic states below

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the photodetachment threshold. Furthermore, the electronic states $A^2\Pi_u$ and $B^2\Sigma_u^+$ are known to have reasonably high Franck-Condon overlap factors with the $X^2\Sigma_g^+$ ground state for the transitions between their lowest vibrational levels $v' = 0 \rightarrow v'' = 0$ [6–8]. Simulations of laser cooling using the $B^2\Sigma_u^+$ [5] and $A^2\Pi_u$ [9] states have shown that C_2^- can in principle be cooled efficiently to millikelvin temperatures using Doppler or Sisyphus cooling in Paul or Penning traps. If laser cooling of C_2^- anions were to be realized, it would open up the possibility of sympathetically cooling other anions [9] or even antiprotons [10], since the efficient production of antihydrogen atoms is being investigated for tests of fundamental physics such as *CPT* invariance [11] and the weak equivalence principle [12].

The diatomic molecular anion C_2^- has been a model system for decades, attracting a great deal of experimental [13–27] and theoretical [8,28–36] interest. Its electronically excited states [32] are still bound states, a feature that is unusual for an anion and which is a consequence of the high electron affinity (EA) of neutral C_2 (around 3.3 eV [17,21]) in combination with the open-shell character of the electronic configuration of carbon dimer. In its ground electronic state ($X^2\Sigma_g^+$) the molecule has only evenly numbered rotational states due to the nuclear statistics of the $^{12}C_2^-$ molecule with zero spin nuclei, while in the excited $B^2\Sigma_u^+$ state, only odd-numbered rotational states exist.

Furthermore, the C_2^- anion could also be present in astrophysical environments since the neutral C_2 is abundant in interstellar space [37] and in comet tails [38] and is a common component of carbon stars [39,40]. The large EA of C_2 and strong electronic absorption bands of C_2^- [16] could make the anion detectable in space [41] but as yet, also due to its lack of a permanent dipole moment, no conclusive evidence of its presence has been found [42–44]. Its most abundant isotopologue $^{12}C_2^-$ is a homonuclear diatomic molecule which does not exhibit a pure rovibrational spectrum, thus making difficult detection in emission of this anion.

Laser cooling of C_2^- would ideally start with ions initially cooled to around 10 K, for example, by helium buffer gas cooling in a cryogenic ion trap [45,46]. Processes used to generate C_2^- involve applying an electric discharge to a mixture of C_2H_2 and CO_2 in a carrier gas [25,47] which may form the anion in its excited vibrational states. Besides cooling the translational motion, the buffer gas is then also required to cool the internal degrees of freedom via inelastic collisions. Furthermore, the buffer gas may be a useful tool to quench excited vibrational levels when they get populated during laser cooling due to the nondiagonal Franck-Condon factors. This could circumvent the need for additional repumping lasers. In a similar scheme, rotational buffer gas cooling was performed during sympathetic translational cooling of MgH^+ [48].

In a recent paper we reported cross sections and rate coefficients for C_2^- -He rotationally inelastic collisions, treating the anion as a rigid rotor [49]. The computed rates for rotational excitation and quenching were found to be in line with those for similar ionic species interacting with helium [46]. Simulations of cooling rotational motion at typical helium pressures in ion traps showed that thermalization to Boltzmann populations occurred within a fraction of a second.

We have extended this work by also modeling the rotational cooling of C_2^- with neon and argon atomic partners [50]. It was found that thermalization times of C_2^- with He and Ne were fairly similar, but cooling was significantly faster with Ar. This is obviously due to the increased interaction strength between C_2^- and the largest atom in the series $He < Ne < Ar$. Then we additionally investigated rovibrational inelastic rate coefficients of the present title anion with He, Ne and Ar [51], showing that such energy-exchange processes carry fairly small probabilities for He and Ne, while the Ar partner produces the largest inelastic rates along the series.

In a recent experimental investigation of the rovibrational quenching processes in collision with H_2 [52], we compared the measured experimental rate coefficient value with quantum calculations in which the molecular hydrogen partner was treated as a structureless object, thereby reducing the number of dimensions of the interaction potential energy surface (PES) to three. Since the agreement of the calculations with experiment turned out to be inadequate, we have now extended the number of dimensions of the required PES to five, as mentioned earlier and as discussed in the next section. Therefore, we present in this work different features of the interaction forces, together with additional quantum calculations of the relevant inelastic cross sections and inelastic rate coefficients. The concurrent rotational excitation processes involving the H_2 will also be presented and discussed.

As C_2^- has no oscillating dipole moment, the vibrational levels are long-lived, with the ground electronic state's $v = 2$ levels persisting for over 5 s [24], and so collisions are the only viable efficient means of quenching these states. The rate coefficients for C_2^- vibrational quenching with H_2 may also prove useful in future astrophysical studies, should the anion be detected in an interstellar environment where excited vibrational states are important for observation, as would be the case in the circumstellar envelope around carbon-rich stars where molecular hydrogen is also abundant.

The paper is organized as follows. In Sec. II we discuss the calculations carried out for the *ab initio* multidimensional potential energy surface for the C_2^- in its ground electronic ($^2\Sigma_g^+$) state interacting with the H_2 molecule, also in its ground electronic state. We provide details of the *ab initio* five-dimensional (5D) PES and describe the fitting via a neural network generated functional form to the raw original points. This section also contains details of the vibrationally averaged matrix elements required for scattering calculations. The close-coupled scattering calculations that we employ in this study are described in Sec. III. Cross sections and corresponding rate coefficients for rotationally and vibrationally inelastic collisions are presented in Sec. IV, as well as test calculations on the robustness of the present results. We summarize our present findings in Sec. V, where we also report our conclusions.

II. C_2^- ($X^2\Sigma_g^+$) INTERACTING WITH THE H_2 MOLECULAR PARTNER: DETAILS OF THE 5D POTENTIAL ENERGY SURFACE

As discussed recently by Gulania *et al.* [36], the electronic structure of the C_2 molecule is notoriously difficult to calculate accurately due to many low-lying electronic states giving

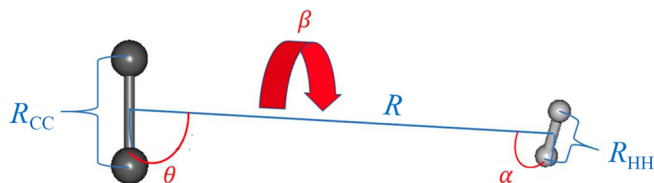


FIG. 1. Graphical representation of the five active coordinates employed to generate the 5D PES of the present system. The distance between the center of mass of C_2^- and that of H_2 is the radial distance R . The two bond distances are R_{CC} and R_{HH} , but only the former is kept as a variable. The three angles are defined in the text. See the text for further details.

rise to a multireference character of the *ab initio* description of its ground electronic state. For the C_2^- anion considered here, the situation is not so severe, but the presence of a closely lying $A^2\Pi_u$ state [4000 cm^{-1} above the ground ($^2\Sigma_g^+$) state] still makes electronic-structure calculations challenging. The interaction energies between C_2^- in its ground electronic state and the H_2 molecular partner in its ground electronic state are calculated to map the full 5D PES as a function of the five independent variables pictorially shown in Fig. 1. We use *ab initio* methods as implemented in the MOLPRO suite of codes (version 2022.2) [53,54]. Geometries of the C_2^- - H_2 system are defined on a Jacobi grid as illustrated in Fig. 1. In the calculations, the value of R ranges between 2.6 and 25.0 Å (the choice of grid points varies with the angles and the R_{CC} bond length). The θ , β , and α angles are defined between R and the two internuclear bond axes R_{CC} and R_{HH} , as shown in the graphic in Fig. 1. For the angle θ , values at intervals of 10° from 0 to 90° are used. For the β angle four values at intervals of 30° between 0 and 90° are used. Finally, for the angle α , we employ seven values between 0 and 180° at intervals of 30° . The values of the C-C bond length are varied between 1.18 and 1.50 Å (1.18, 1.22, 1.24, 1.2689, 1.28, 1.30, 1.35, 1.40, 1.45, and 1.50 Å), including the equilibrium value of $R_{CC\text{eq}} = 1.2689$ Å. This is sufficient to cover the vibrational levels of C_2^- of interest in the present study.

More specifically, we deal mainly with the transition involving the $\nu = 1$ to $\nu = 0$ vibrational levels of C_2^- , with an energy difference calculated by us to be about 1754 cm^{-1} , a value not far from the experimental gap of 1757 cm^{-1} as discussed in our earlier work [52]. Our computed rotational constant is $B_e = 1.729$ cm^{-1} (see a comparison with other data in our earlier work in [52]). Interaction energies between C_2^- and the H_2 partner are determined by subtracting the asymptotic energies for each R_{CC} value. Because the energy separation between the lower vibrational levels of the hydrogen molecular partner is two to three times larger than those of the anion, we expect that its vibrational excitation probabilities of interest in this study will be much smaller than those for the anion, especially for the temperatures considered in this work ($T \leq 100$ K). Furthermore, the energy spacing between the $j_2 = 0$ and 2 levels of *para*-hydrogen is around 500 K. Hence, we disregard the vibrational coordinate ($r_2 = R_{HH}$) of the neutral partner indicated in Fig. 1. On the other hand, we include the dynamics of concurrent rotational excitations of the H_2 partner in some of our calculations.

TABLE I. Summary of the ANN fits obtained for the C_2^- - H_2 system.

Fit	Training Data (%)	Neural Network	RMSD (cm^{-1})	
			Test	Training
1	60	(40,40)	63.49	2.10
2	70	(40,40)	411.8	2.56
3	80	(40,40)	298.94	1.55
4	90	(40,40)	36.36	2.88
5	90	(50,50)	71.15	3.66
6	90	(60,60)	154.23	0.783
7	90	(50,40,40)	28.72	0.70
8	90	(50,50,40)	21.51	0.70
9	90	(50,50,50)	9.05	0.70

The potential energy values for the system are calculated using the restricted coupled-clusters single-, double-, and perturbative triple-excitation method [55,56], including relativistic corrections [57]. An aug-cc-pVQZ basis set [58] is used on each carbon center and an aug-cc-pV5Z basis set for the H atoms.

A. Artificial neural network fitting of the 5D raw points

The 5D *ab initio* data are then fitted using the artificial neural network (ANN) method (for extended documentation on the method see [59–61]). The data set consists of 76 474 points (the number of original raw points computed in the five independent variables described earlier was a bit larger, 76 634; it was slightly reduced to improve the smoothness of their representation). That set of points covers an energy range from -723.81 to $10\,997.2$ cm^{-1} . The Levenberg-Marquardt algorithm along with the Bayesian regularization method is used to adjust the neural network parameters. The activation functions are chosen to be modified sigmoid functions given as

$$\sigma(a) = 2/[1 + \exp(-2a)] - 1. \quad (1)$$

The target mean-square error is set at 0.5 cm^{-1} and the ANN is trained for a maximum of 4000 epochs. The data set is partitioned into training and test data sets. Different fits are obtained using a two-layer (40, 40) network, where the numbers indicate the chosen number of nodes in each layer. We then vary the training-to-test ratio from 60:40 to 90:10. It is found that the 90:10 ratio gives the best root-mean-square deviation (RMSD) of 36.36 cm^{-1} for the test data. A further increase in the number of nodes does not improve the quality of the fit. To improve the fit, different fits with three-layer networks are attempted for a 90:10 training-test ratio. The best fit (fit 9) is obtained by a (50, 50, 50) network that results in an RMSD of 0.70 cm^{-1} for the training set and an RMSD of 9.05 cm^{-1} for the test data. A summary of the ANN fits is given in Table I.

The maximum deviation is found to be 693.58 cm^{-1} , which occurs for an energy of 7618.85 cm^{-1} . It should be noted that for the energy range considered in the quantum dynamical study reported below, this deviation is not consequential. The ANN PES thus obtained is found to be smooth without overfitting issues.

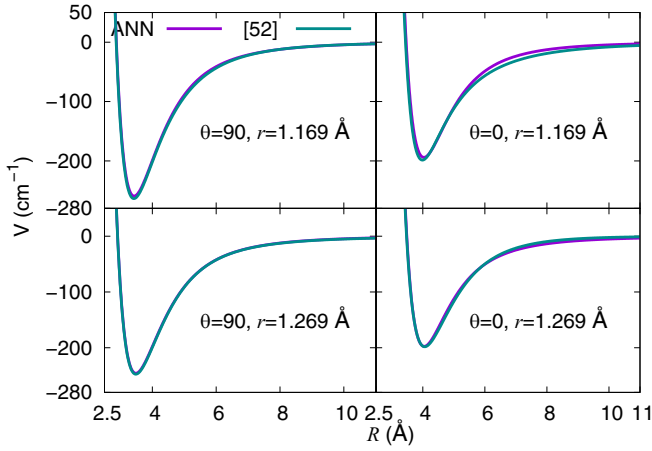


FIG. 2. Graphical representation of a comparison between the calculations of the present work (the ANN results) and the earlier 3D results reported by some of us in Ref. [52]. See the text for further details.

After having presented in the earlier part of this section the details of the ANN fitting of the initial raw points generated for the 5D PES discussed earlier, it is interesting to see how our results compare with the earlier evaluation in three dimensions [52]. To this end, we show in Fig. 2 a reduction to three dimensions of the present 5D PES with a further comparison with the same data from our earlier paper [52]. We indicate in the four panels two different bond lengths of the vibrating C_2^- for two different angular orientations of the H_2 partner, treated in both cases as a pointlike structure. It is clear from the comparison in the figure that the present results reproduce very well the earlier calculations, a reassuring feature which confirms the quality of the present study treating the interaction forces in five dimensions.

To further verify the quality of the ANN fit, we check in detail the range of the C-C bond length for which the ANN expansion has sufficient angular and internuclear distance points. We actually find it to be expedient to constrain the ranges of the original configurations to avoid nonphysical features in the resulting 5D interaction for R_{CC} distances larger than 1.4 Å. The effects of such numerical limitations to help in data smoothness are reported in three sets of panels of Fig. 3, which show how we produce in the end smooth-behaving angular cuts for a variety of angles in the fuller 5D interaction potential.

Since C_2^- does not have a permanent dipole moment, the dominant terms in the long-range potential are related to the polarizability of H_2 in its equilibrium bond distance,

$$V_{LR} = -\frac{\alpha_0}{2R^4} + \left(\frac{2\alpha_2}{R^4}\right)P_2(\cos\alpha), \quad (2)$$

where $\alpha_0 = (\alpha_{\parallel} + 2\alpha_{\perp})/3$ and $\alpha_2 = \alpha_{\parallel} - \alpha_{\perp}$, with $\alpha_{\parallel}$ and $\alpha_{\perp}$ the parallel and perpendicular components, respectively, of H_2 . The angle α is the orientation angle given in Fig. 1.

The polarizability for H_2 at $r_2 = 1.4a_0$ (0.7408 Å) is given by $\alpha_0 = 5.1786a_0^3$ and $\alpha_2 = 1.8028a_0^3$ [52]. For comparison, $\alpha_0 = 1.41a_0^3$ for He (see [62]).

We can therefore employ the above expression of the long-range extension of the interaction, the V_{LR} , to bring

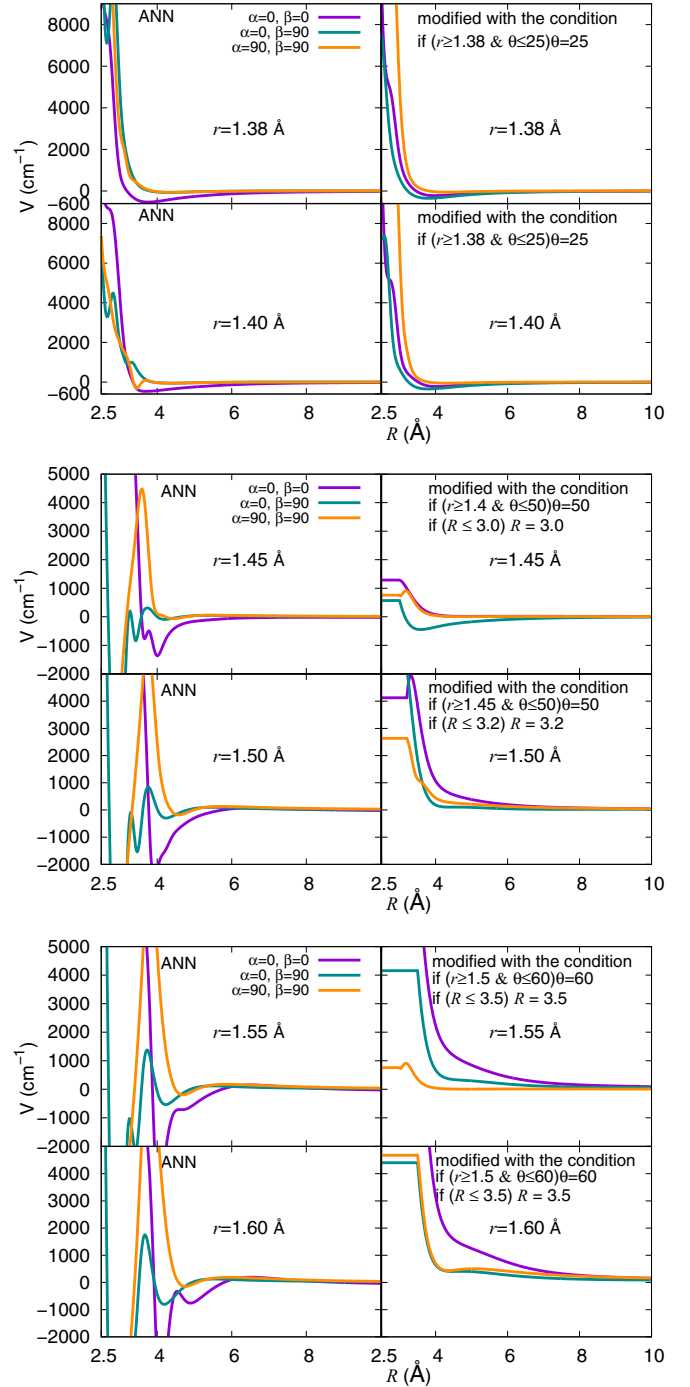


FIG. 3. Graphical representation of the results on the constrained ANN fitting for different bond lengths of the anion and for different selections of the three angles of the full 5D PES. See the text for further details.

the ANN fitted 5D PES to larger radial distances. We show in Fig. 4 the effects of such a propagation to larger distances for the present ANN potential fit. We see from the reported examples in the two panels that merging the two sets of points at distances of the order of about 24.0 Å provides a smooth transition to the interaction at long distances, as shown by the curves in yellow labeled VNNLR.

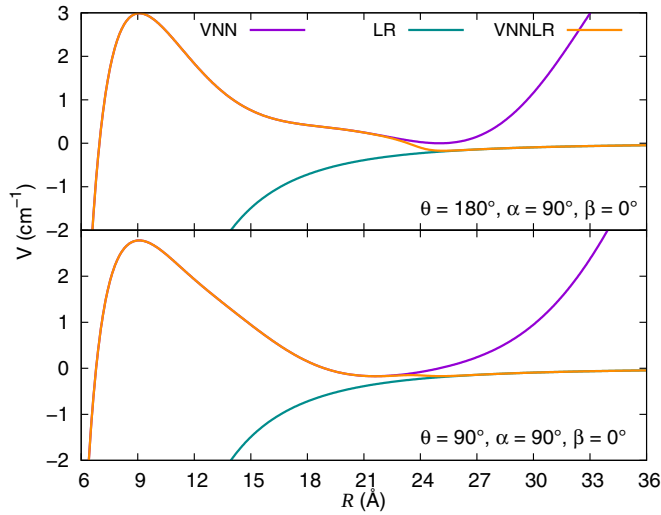


FIG. 4. Graphical representation of the extended range of the 5D interaction using the long-range (LR) formulas (2)–(4). See the text for further details.

The final form of the potential V_f using a switching function is given by

$$V_f = f_s V_{\text{ANN}} + (1 - f_s) V_{\text{LR}}, \quad (3)$$

where the switching function $f_s(R)$ is

$$f_s(R) = \frac{1}{e^{\frac{(R-R_0)}{\Delta x}} + 1}, \quad (4)$$

with $R_0 = 24.0 \text{ \AA}$ and $\Delta x = 0.5 \text{ \AA}$. Additional information on the fitted 5D PES is given in Ref. [63].

B. Calculations of the coupling vibrational matrix elements within the 5D PES

The scattering calculations described in the next section require the interaction potential to be represented using an extended angular basis as

$$V(R, r_1, \theta, \alpha, \beta) = \sum_{\lambda_1, \lambda_2, \lambda} A_{\lambda_1, \lambda_2, \lambda}(r_1, R) Y_{\lambda_1, \lambda_2, \lambda}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \hat{\mathbf{R}}), \quad (5)$$

where $Y_{\lambda_1, \lambda_2, \lambda}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \hat{\mathbf{R}})$ is a bispherical harmonics function given by

$$Y_{\lambda_1, \lambda_2, \lambda}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \hat{\mathbf{R}}) = \sum_{m_{\lambda_1}, m_{\lambda_2}, m_{\lambda}} \langle \lambda_1, m_{\lambda_1}, \lambda_2, m_{\lambda_2} | \lambda, m_{\lambda} \rangle \times Y_{\lambda_1}^{m_{\lambda_1}}(\hat{\mathbf{r}}_1) Y_{\lambda_2}^{m_{\lambda_2}}(\hat{\mathbf{r}}_2) Y_{\lambda}^{m_{\lambda}}(\hat{\mathbf{R}}), \quad (6)$$

where $0 \leq \lambda_1 \leq 8$, $0 \leq \lambda_2 \leq 4$, and only even values of λ_1 and λ_2 are retained due to the symmetry of C_2^- and H_2 . The next step in the representation of the interaction potential requires construction of matrix elements coming from the convolution of the potential in Eq. (2) over the asymptotic vibrational wave functions of the C_2^- partner

$$V_{\nu\nu'}(R, \theta, \alpha, \beta) = \langle \chi_{\nu}(r_1) | V(R, r_1, \theta, \alpha, \beta) | \chi_{\nu'}(r_1) \rangle. \quad (7)$$

The off-diagonal $V_{01}(R, \theta, \alpha, \beta)$ term is the coupling which directly drives vibrationally inelastic $\nu = 1$ to $\nu = 0$

transitions. At short distances R , the coupling terms are repulsive, becoming negligible quickly at longer distances, as is the case for many other atom-diatom systems. This can also be seen for C_2^- interacting with the H_2 partner as a pointlike partner presented in our earlier work [52]. We will further discuss this point below, where we show that the close-coupling scattering calculations discussed in the next section require the vibrationally labeled coupling matrix elements to be further written in the form of a multipole expansion as

$$V_{\nu\nu'}(R, \theta, \alpha, \beta) = \sum_{\lambda_1, \lambda_2, \lambda}^{\lambda_{12 \max}} V_{\nu\nu'}^{\lambda_1, \lambda_2, \lambda}(R) Y_{\lambda_1, \lambda_2, \lambda}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \hat{\mathbf{R}}), \quad (8)$$

where again, due to C_2^- being a homonuclear diatom, only even λ terms are required. The bispherical harmonic functions are defined in Eq. (4) above.

To carry out additional tests on the reliability of the present evaluation of the vibrational coupling matrix elements, we have tried to reproduce the reduced-dimension results from our earlier work [52] where the 3D PES was employed, as discussed earlier in the Introduction, by using instead the calculated matrix elements with the full 5D interaction but scaling them within the 3D representation of the earlier work. A comparison of the present results with those from [52] is presented in Fig. 5. We show in Fig. 5(b) the off-diagonal expansion coefficients V_{01}^{λ} for the first three values of the single λ expansion index used in three dimensions: Each of them compacts the three different indices for the 5D case that we have discussed before. The results in Fig. 5(a) compare the same type of results but for the diagonal matrix element V_{00}^{λ} . We notice, first of all, that all the terms in Fig. 5(b) quickly approach zero as R is increased, indicating the essentially short-range nature of the vibrational coupling matrix elements between the two lower levels. Additionally, all three multipolar coefficients of the $V_{01}^{\lambda}(R)$ matrix element are steeply repulsive as R decreases. The solid lines show the 3D coefficients reproduced via the present ANN expansion, while the dashed lines are our earlier results from the 3D calculations. On the whole, we can see that the general shape of these coupling matrix elements follows what we had found in the earlier study and are well reproduced by the constrained representation of the 5D interaction once reduced to the 3D version.

The diagonal matrix elements given in Fig. 5(a) show some quantitative differences between the present findings (solid lines) and the earlier results (dashed lines): The scaled 5D diagonal terms are somewhat smaller in strength than the earlier calculations in three dimensions. This result indicates that the use of a higher-dimensional PES, as in the present case, distributes the anisotropic features over a larger angular range, which is therefore affected by the scaling into the reduced dimensionality. On the other hand, the off-diagonal coupling terms in Fig. 5(b) act on a much shorter range of radial values and therefore sample a very similar angular anisotropy in both surfaces. This is a reassuring finding since our present study is chiefly directed to testing state-changing vibrational processes, dominated by the off-diagonal matrix elements of the coupling potential.

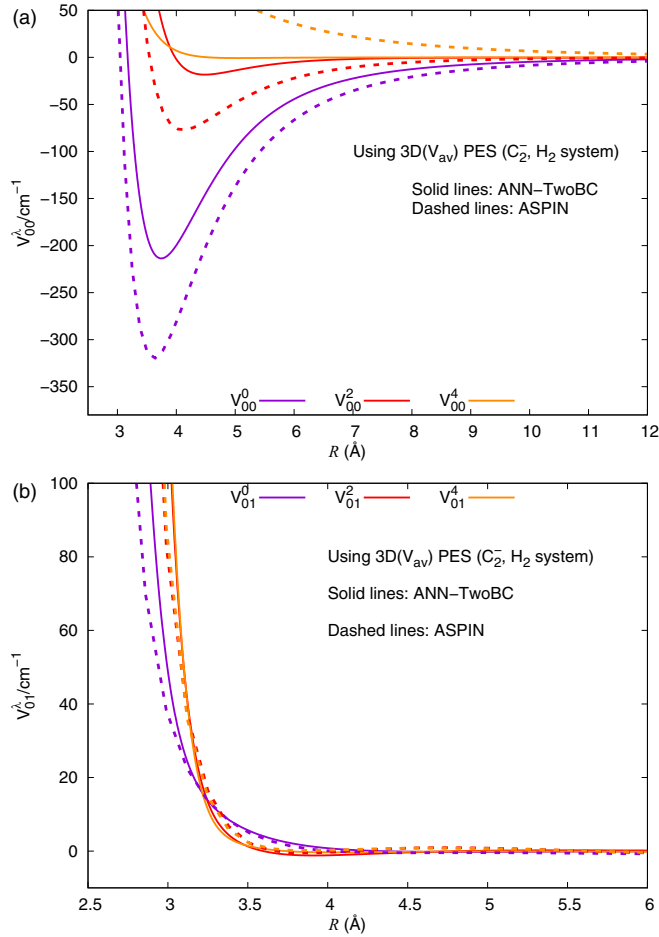


FIG. 5. Comparison of coupling matrix elements obtained from the present ANN fitting from the 5D original points using the TWOBC code (solid lines) with those obtained from our earlier work of [52] using the ASPIN code (dashed lines): (a) diagonal coupling between the $v = 0$ levels and (b) coupling between the $v = 0$ and 1 levels. Each curve corresponds to a different value of the expansion index λ , as a superscript and as given in Eq. (5). See the text for further details.

III. QUANTUM SCATTERING CALCULATIONS

Quantum scattering calculations are carried out using the coupled-channel (CC) method to solve the Schrödinger equation for scattering between two vibrating and rotating diatomic molecules as implemented in the TWOBC code developed by Krems [64]. The method has been described in detail before [65,66] and only a brief summary is given here, with the equations given in atomic units. For a given total angular momentum $\mathbf{J} = \mathbf{l} + \mathbf{j}_{12}$, where $\mathbf{j}_{12} = \mathbf{j}_1 + \mathbf{j}_2$, the latter two rotational angular momenta pertaining to the two interacting molecular rotors, while $\mathbf{l}$ describes the relative angular momentum between partners.

Then the scattering wave function is expanded as

$$\Psi^{JM}(R, r_1, \theta, \alpha, \beta) = \frac{1}{R} \sum_{v,k} f_{vk}^J(R) \chi_{v,j_1}(r_1) \times Y_k^{JM}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \hat{\mathbf{R}}), \quad (9)$$

where $k = \{j_1, j_2, j_{12}, l\}$. The $\chi_{v,j_1}(r_1)$ are the radial parts of the rovibrational eigenfunctions of the anionic molecule taking part in the collisions, while the $f_{vk}^J(R)$ are the radial expansion functions which need to be determined (see Ref. [64]).

Substituting the expansion into the Schrödinger equation with the Hamiltonian for diatom-diatom scattering [64–66] leads to the CC equations for each J :

$$\left(\frac{d^2}{dR^2} + \mathbf{K}^2 - \mathbf{V} - \frac{\mathbf{l}^2}{R^2} \right) \mathbf{f}^J = 0. \quad (10)$$

Here each element of $\mathbf{K} = \delta_{i,j} 2\mu(E - \epsilon_i)$ (where ϵ_i is the channel asymptotic energy and μ is the reduced mass of the system), $\mathbf{V} = 2\mu\mathbf{U}$ is the interaction potential matrix between channels, and $\mathbf{l}^2$ is the matrix of orbital angular momentum. For the rovibrational scattering calculations of interest here, the matrix elements $\mathbf{U}$ are given explicitly as

$$\begin{aligned} \langle v j k J | V | v' j' k' J \rangle &= \int_0^\infty dr_1 \int d\mathbf{r}_1 \int d\mathbf{r}_2 \int d\hat{\mathbf{R}} \\ &\times \chi_{v,j_1}(r_1) Y_k^{JM}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \hat{\mathbf{R}}) V(R, r_1, \theta, \alpha, \beta) \chi_{v',j'_1}^*(r_1) \\ &\times Y_{k'}^{JM}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \hat{\mathbf{R}}), \end{aligned} \quad (11)$$

where the angular functions are those defined right after Eq. (4).

Since the intermolecular potential $V(R, r_1, \theta, \alpha, \beta)$ is expressed as in Eq. (7), the matrix elements can now also be written as

$$\langle v j k J | V | v' j' k' J \rangle = \sum_{\lambda_1, \lambda_2, \lambda} V_{v v'}^{\lambda_1, \lambda_2, \lambda}(R) f_{\lambda_{12} j_1 k j'_1 k'}^J, \quad (12)$$

where the $f_{\lambda_{12} j_1 k j'_1 k'}^J$ terms are the Percival-Seaton coefficients given as

$$\begin{aligned} f_{\lambda_{12} j_1 k j'_1 k'}^J &= \int d\hat{\mathbf{r}}_1 d\hat{\mathbf{r}}_2 \int d\hat{\mathbf{R}} Y_k^{JM}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \hat{\mathbf{R}})^* \\ &\times P_\lambda(\cos \theta) Y_{k'}^{JM}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \hat{\mathbf{R}}), \end{aligned} \quad (13)$$

for which analytical forms are known [66]. Equation (12) also makes use of the widely known approximation

$$V_{v, v'}^{\lambda_1, \lambda_2, \lambda}(R) \approx V_{v j_1 v' j'_1}^{\lambda_1, \lambda_2, \lambda}(R) \quad (14)$$

for all j_1 such that the effect of rotation on the vibrational matrix elements is ignored. Their actual excitation within the vibrational cooling dynamics will however be treated exactly.

The CC equations are propagated outward from the classically forbidden region to a sufficiently large distance where the scattering matrix $\mathbf{S}$ can be obtained. The actual numerical details will be given below.

The rovibrational state-changing cross sections are obtained as

$$\begin{aligned} \sigma_{v j_1 j_2 \rightarrow v' j'_1 j'_2}(E_{\text{coll}}) &= \frac{\pi}{(2j_1 + 1)(2j_2 + 1)k_{v j_1 j_2}^2} \sum_J (2J + 1) \\ &\times \sum_{j_{12}, j'_{12}, l, l'} |\delta_{v j_1 j_2 l j_{12}, v' j'_1 j'_2 l' j'_{12}} \\ &- S_{v j_1 j_2 l j_{12}, v' j'_1 j'_2 l' j'_{12}}^J(E_{\text{coll}})|^2, \end{aligned} \quad (15)$$

where E_{coll} is the collision energy. In all scattering calculations the C_2^- anion is treated as a pseudosinglet $^1\Sigma$ and the effects of spin-rotation coupling are ignored. In our previous work on this system it was shown that a pseudosinglet treatment of the rotational state-changing collisions resulted in essentially the same results as the explicit doublet calculation when the relevant cross sections were summed [49]. This approximation reduces the computational cost of the scattering calculations without significantly affecting the size of the cross sections and thus the present conclusions.

For the CC equations to converge, a rotational basis set is used which includes up to $j_1 = 20$ rotational functions for each vibrational state and for either the ortho- H_2 or para- H_2 collision partners. The CC equations are propagated along R between 1.7 and 1500.0 Å using the Johnson logarithm-derivative matrix propagation [67]. The potential energy is calculated to generate the $V_{\nu\nu',\lambda_2,\lambda}(R)$ values using our long-range correction discussed earlier and then employed directly as such within the TWOBC code employed in our calculations [64]. Our *ab initio* calculated interaction energies are computed to $R = 41$ Å, a distance where the interaction energy is expected to be fairly negligible for the temperature of interest here. In any case, we carry out the potential extrapolation using our long-range terms to much larger R values (see above) to make sure that by that distance the extrapolated PES would have a negligible effect on the computed cross sections [49].

A number of parameters of the calculation are checked for convergence. The number of $\lambda_1, \lambda_2, \lambda$ terms from Eq. (10) is checked for both rotationally and vibrationally inelastic collisions. For the former, calculations are converged to better than 1% using only three terms (up to $\lambda = 4$). For vibrationally inelastic collisions the convergence with increasing $\lambda_1, \lambda_2, \lambda$ is less precise. This is due to the very small cross sections for these processes, which makes obtaining precise and stable values more difficult to achieve. For production calculations, more than 20 ($\lambda_1, \lambda_2, \lambda$) terms are included for each $V_{\nu\nu'}(R)$.

Despite this practical difficulty, the vibrationally inelastic cross sections remain reasonably consistent and thus our R range is sufficiently large to obtain cross sections which are to the correct order of magnitude, sufficient to assess rates for vibrational quenching of C_2^- in collision with H_2 .

As a final check of our calculation parameters, the effect of the vibrational basis set is also considered. In all calculations we use the vibrational energies and rotational constants obtained from calculations using the software LEVEL, as discussed in [52], and employing our own C_2^- potential energy curve as discussed in our earlier work [52]. It is found that for $\nu = 0$ and 1, which are the states of interest here (see the next section), it is sufficient to only include these two asymptotic vibrational states.

Scattering calculations are carried out for collision energies between 1 and 1500 cm^{-1} using steps of 0.1 cm^{-1} for energies up to 11 cm^{-1} , 1.0 cm^{-1} for 11–50 cm^{-1} , 2 cm^{-1} for 50–100 cm^{-1} , and 5 cm^{-1} for 100–200 cm^{-1} . Then we use steps of 10.0 cm^{-1} for intervals from 200 to 400 cm^{-1} , steps of 20.0 cm^{-1} for the range from 400 to 700 cm^{-1} , steps of 50 cm^{-1} for the range from 700 to 1000 cm^{-1} , and steps of 100 cm^{-1} for the final energy range from 1000 to 1500 cm^{-1} . This fine energy grid is used to ensure that important features

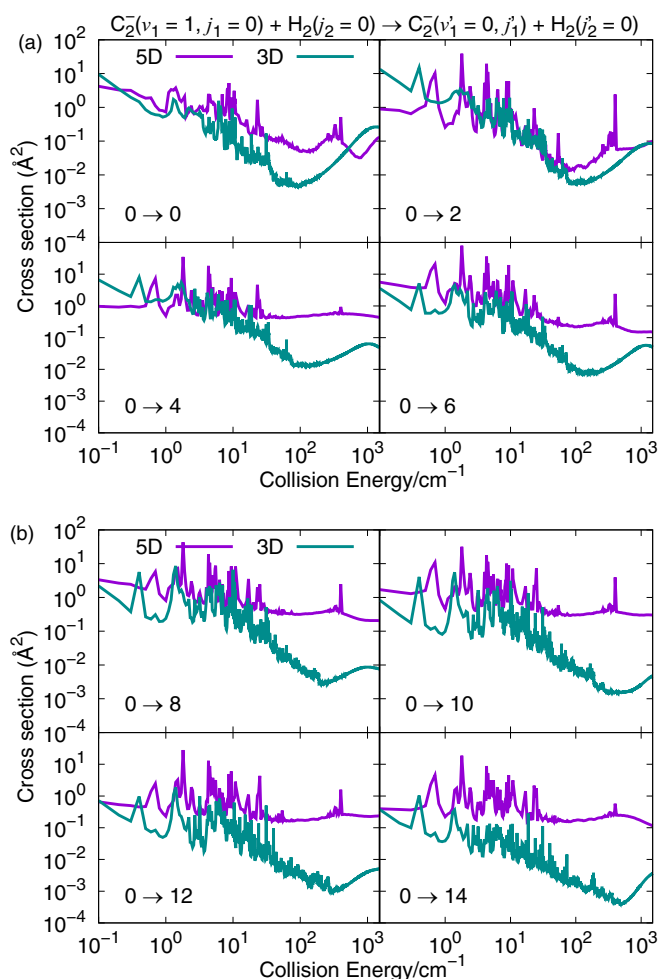


FIG. 6. Comparison of computed rotationally inelastic cross sections accompanying the vibrational deexcitation of the anion using either the full 5D interaction potential (purple curves) or the reduced 3D interaction potential described in [52] (green curves). The collision partner is the para- H_2 neutral molecule. The labeling within each panel refers only to the initial and final rotational states of the molecular anion before and after its vibrational cooling. (a) Transitions between the lowest four levels and (b) transitions to four higher levels. See the text for further details.

such as resonances appearing in the cross sections are accurately accounted for and their contributions correctly included when the corresponding rates are calculated. The number of partial waves is increased with increasing energy up to $J = 80$ for the highest energies considered.

IV. RESULTS AND DISCUSSION

A. Rovibrational inelastic cross sections of the anionic partner

To analyze as extensively as possible the differences in the dynamical behavior of the title system when the full dimensionality of the 5D PES is employed, we start by presenting in Fig. 6 the computed inelastic cross sections using both the 5D interaction potential and the 3D interaction discussed in our earlier work [52]. The different coloring for the two sets of calculations is explained in the caption to Fig. 6.

The two sets of four panels of Fig. 6 report eight different rotational transitions accompanying the vibrational deexcitation for the anionic rotor, while the para- H_2 partner is left in its ground rotational state ($j_2' = 0$). The main vibrational state-changing process is the same for all the reported curves and therefore not indicated in their labels; it involves the $v = 1$ to $v = 0$ deexcitation process. First, we clearly see in all panels that using the more accurate 5D representation of the interaction produces inelastic cross sections that are invariably larger than those obtained in our previous work using the 3D interaction. This is particularly evident at higher collision energies, where the size differences can be as large as more than two orders of magnitude. Additionally, we see in the low-energy range that a large number of narrow resonant structures appear, as expected for the present interaction between light partners. Since our primary interest in the present work involves the comparative sizes of the inelastic rate coefficients, discussed later in the paper, we do not further carry out a detailed analysis of such resonant features; none of them has been directly revealed in the existing experiments so far. On the other hand, we do make sure that our energy grid is fine enough to include all the peak regions of the cross sections, since it is important to have them correctly represented for later calculating the inelastic rate coefficients (see below). It is significant to note that the top left panel of Fig. 6(a) indicates the purely vibrational deexcitation channel, since both colliding rotors are left in their ground rotational state. We clearly see that the purely vibrationally inelastic data are very close in size for both calculations, with the 5D results becoming larger than the 3D data at collision energies of about 10 cm^{-1} and above.

Figure 6(b) presents the same set of processes as those discussed before, but involving this time the higher-lying rotational states of the C_2^- partner. One marked difference from the earlier data in Fig. 6 is that although the 5D dynamics still produces larger cross sections (purple curves), they are more consistently so, especially in the low-energy range where differences of more than one order of magnitude can be observed. Figure 6 also makes clear the fairly small values of the involved inelastic processes, dominated by the vibrational relaxation channel, some of which become even smaller as the collision energy increases above 10 cm^{-1} . The present data show a broadening of the size range as one moves to higher collision energies, where we see that the larger the rotational energy transfer, the smaller the corresponding cross sections.

A more directly descriptive view of the relative sizes of the various computed cross sections of Fig. 6, as the final rotational state changes, can be seen in the sort of stick spectrum in Fig. 7. We present there three sets of panels, each of them showing the final state distribution at three different collision energies. Figure 7(a) shows $j_1 = 0$ as the initial state, while Fig. 7(b) starts all transitions from $j_1 = 2$. Finally, Fig. 7(c) indicates $j_1 = 4$ as the initial state of all the transitions shown. The following comments can be made from a perusal of these results.

(i) The cross sections in Fig. 7(a) are all uniformly larger than those where the initial state of the anion becomes higher, i.e., $j_1 = 2$ and 4 in Figs. 7(b) and 7(c), respectively.

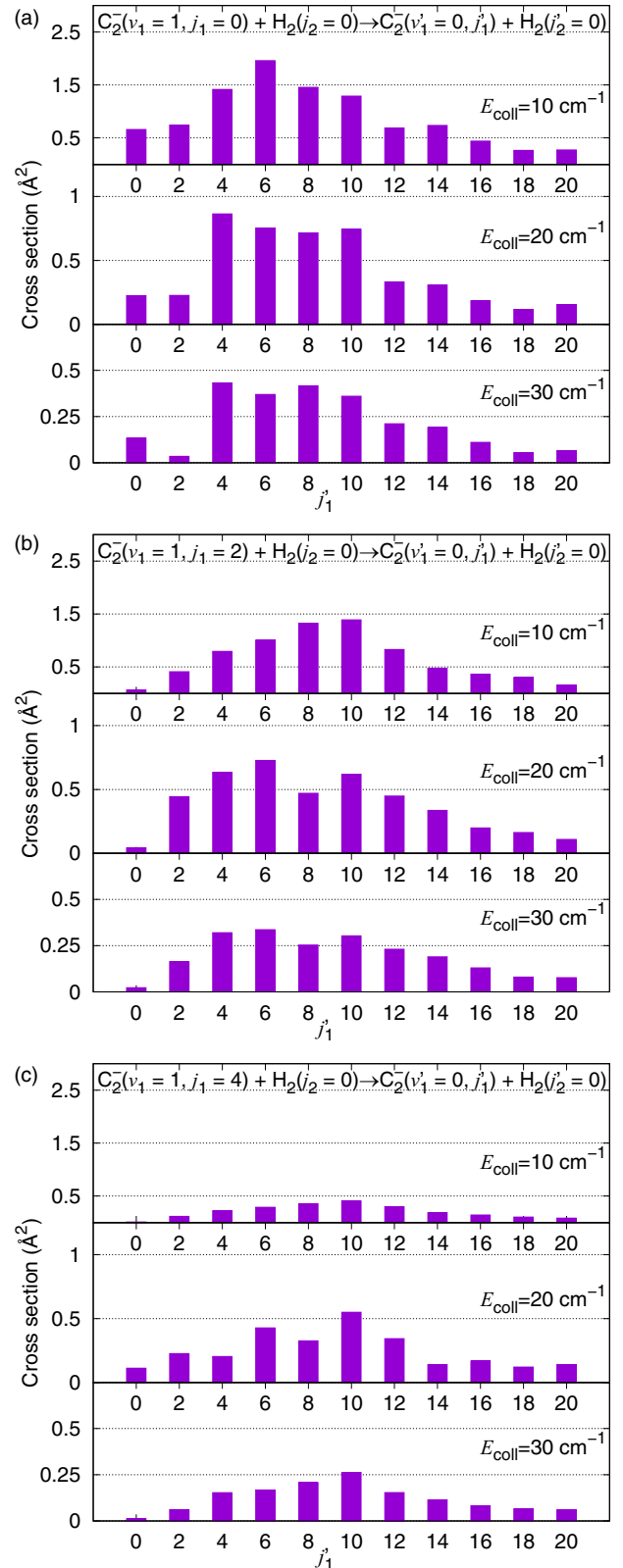


FIG. 7. Same computed inelastic cross sections as in Fig. 6, but here presented as vertical bars for each final rotational state. The neutral molecular partner is again the para- H_2 . The initial state changes in each set of panels: (a) the initial state $j_1 = 0$, (b) the initial state $j_1 = 2$, and (c) the initial state $j_1 = 4$. See the text for further details.

(ii) The reduction in size is most marked for the data in Fig. 7(c), where the cross sections become smaller by nearly one order of magnitude on an average.

(iii) In nearly all the data shown in all three sets of panels we see that the largest excitation probabilities occur for different final rotational states depending on the initial state of the anion before the collision. On the other hand, the amount of angular momentum transferred over the largest cross sections remains in general the same, peaking at $\Delta j_1 = 4$ or 6. The same occurs in all three sets of panels.

(iv) In general, we can also say that the transitions where more units of angular momenta are transferred to rotations yield increasingly smaller cross sections, which become nearly negligible by the time j'_1 becomes equal to 20.

An interesting comparison could be obtained by repeating the calculations shown in Fig. 6, but this time using the ortho- H_2 as the collision partner. In this case the ground rotational state of the neutral molecule is given by $j_2 = 1$; hence we are dealing with a rotating partner that modifies the angular momentum coupling with respect to the case of the para- H_2 , which is a nonrotating collision partner. The results given in Fig. 8 compare our present calculations for the two cases.

The results reported in Figs. 8(a) and 8(b) show the strong similarities between the energy behavior and the relative size of the two different calculations. In all cases we see that the ortho cross sections are either very similar or slightly larger than the para cross sections, this being the case over a broad range of collision energies, while the ortho results yield clearly smaller cross sections as the collision energy increases to about 50 cm^{-1} . The purely vibrationally inelastic data in the topmost left panel in Fig. 8(a) indicate, for this particular case of state-changing dynamics, that the cross sections are nearly coincident with each other, with the para values still exhibiting a more marked presence of resonant peaks.

In the following section we further analyze the effect of rotational excitation in either ortho- or para- H_2 on the vibrational cooling in C_2^- by looking at the behavior of the computed rate coefficients. Additional information and detailed numerical data are given in the Supplemental Material in Ref. [63].

B. Computed rovibrational inelastic rate coefficients

The inelastic cross sections of the preceding section can be used to obtain the corresponding thermal rate coefficients, which can be evaluated as the convolution of the computed inelastic cross sections over a Boltzmann distribution of the relative collision energies of the interacting partners as

$$k_{v j_1 j_2 \rightarrow v' j'_1 j'_2}(T) = \left(\frac{8}{\pi \mu k_B^3 T^3} \right)^{1/2} \int_0^\infty E_{\text{coll}} \sigma_{v j_1 j_2 \rightarrow v' j'_1 j'_2}(E_{\text{coll}}) \times e^{-E_{\text{coll}}/k_B T} dE_{\text{coll}}. \quad (16)$$

As discussed in the Introduction, studies on laser cooling of C_2^- have assumed that the anion was initially cooled to tens of degrees Kelvin [5] and thus the rate coefficients were computed between 5 and 100 K at 1 K intervals. The important contribution of our present detailed calculations will be to assess the individual probabilities of populating by a collision a variety of rotational states of the anion along with the main

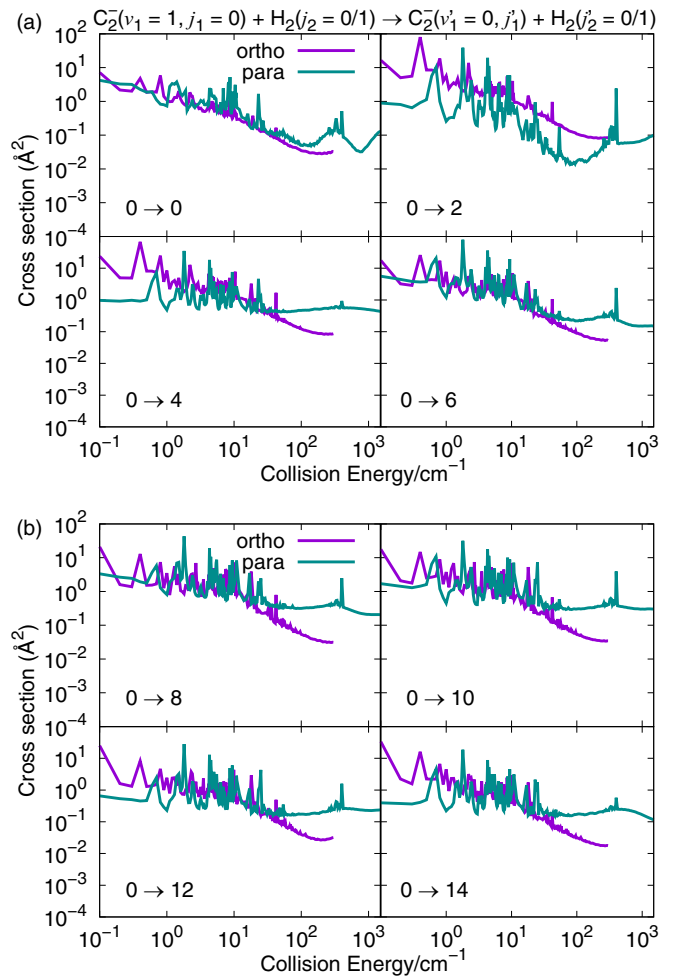


FIG. 8. Comparison of computed rotationally inelastic cross sections accompanying the vibrational deexcitation of the anion using the full 5D interaction potential (purple curves) with the ortho- H_2 as a partner or the earlier results using the para- H_2 as a collision partner. The labeling within each panel refers only to the rotational states of the anion. (a) Transitions between the lowest four levels and (b) transitions to the higher four levels. See the text for further details.

vibrational cooling process. The experiments we described in Ref. [52] in fact were not observing which rotational states would be populated after the anion's decay to its $v = 0$ level in the trap with the H_2 partner, so the computational estimates will be important to know.

To verify once more the effect of using the 5D PES to carry out the relevant inelastic dynamics, we report in the two sets of four panels of Fig. 9 a comparison of the inelastic rate coefficients obtained using the full dynamics (purple lines) and those we had computed in our earlier work [52] for the same range of inelastic processes. All processes are obtained using the para- H_2 as collision partner. The rotational excitation processes involve only states of the anionic partner and correspond to the pure vibrationally inelastic process in the topmost left panels, while all following panels report final populations of higher rotational states of the vibrationally quenched anionic molecule.

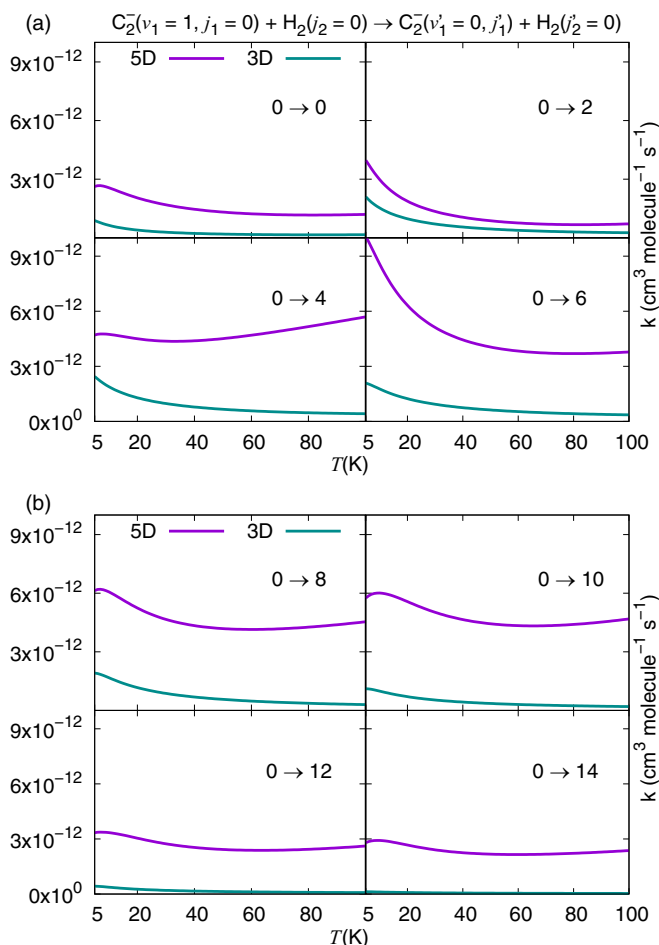


FIG. 9. Computed vibrational cooling rate coefficients of the anion from the $\nu = 1$ level to the $\nu = 0$ level, with concurrent rotational excitation processes as given in each panel. Full calculations using the 5D interaction are shown by purple lines, while the earlier results using the 3D interaction are shown by green lines. Both sets of calculations have the para- H_2 as the collision partner. (a) Transitions to the lower rotational levels of the anion and (b) transitions into higher rotational states of the anion. See the text for further details.

We see in the panels in Fig. 9(a), which correspond to either no energy being transferred to rotational levels or to the smallest amount of energy being transferred to rotation, that the results using the 3D PES (green curves) are very close to the purple curves obtained via the 5D PES at lower temperatures. As more energy is given to rotational excitation the two sets of calculations differ much more from each other in size and in their dependence on temperature. Furthermore, the larger the amount of energy that goes into rotation, the larger the corresponding rate coefficients, a feature of the present findings that we further analyze below.

The calculations reported in Fig. 9(b) analyze the same type of inelastic processes while considering however rotational excitation of the vibrationally quenched anionic partner to higher rotational states: from the $j'_1 = 8$ excitation in the top left panel in Fig. 9(b) to the excitation into $j'_1 = 10, 12$, and 14 in the remaining three panels. In all instances we see that the two sets of rates are more different from each other,

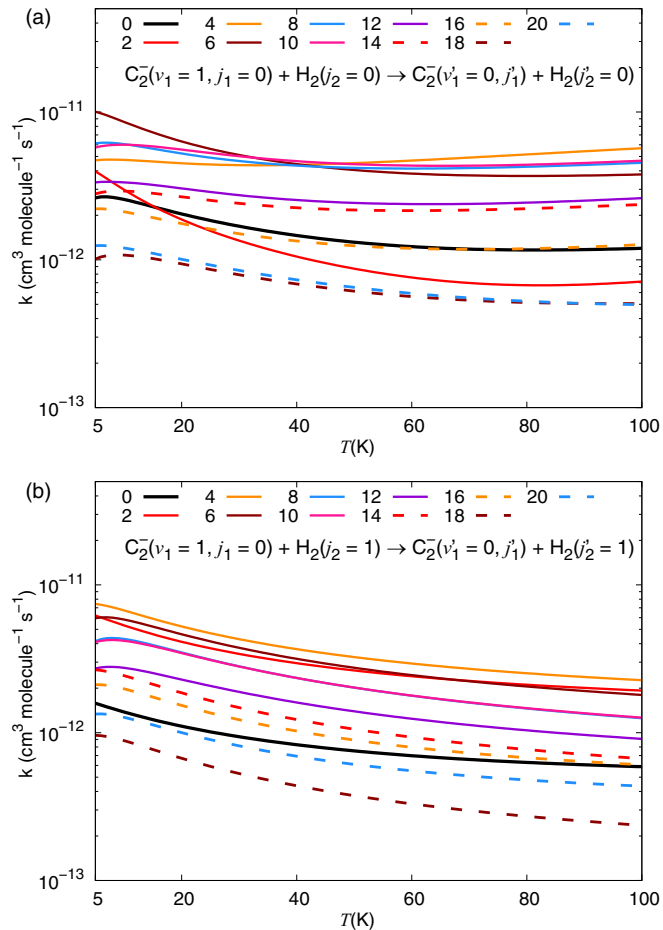


FIG. 10. Plot of the (5D) computed rate coefficients for inelastic processes involving only the molecular anion with (a) the para- H_2 as a partner and (b) the ortho- H_2 as a neutral partner. See the text for further details.

indicating that the data from the purple curves are larger by a factor of 10 than those given by the green curves. In all panels the results of the purple curves are larger than those for purely vibrational transfer shown in the topmost left panel of Fig. 9(a).

Initially, this may appear counterintuitive. However, one realizes that the overall amount of energy being transferred away from the molecule diminishes as the higher rotational state of the vibrationally quenched ($\nu' = 0$) state of C_2^- becomes populated. While the $0 \rightarrow 0$ transition corresponds to a loss of 1754 cm^{-1} , the successive higher j'_1 transitions ($0 \rightarrow 2, 0 \rightarrow 4, \dots, 0 \rightarrow 14$) involve an increasing amount of energy being kept as internal rotational energy, with the actual amount of energy transferred away becoming less ($1754 - 1.729[j'_1(j'_1 + 1)]$) and the degeneracy of the j'_1 state increasing as $2j'_1 + 1$. Hence, we could see that the reduction of the amount of energy being dissipated causes greater efficiency for the internal energy redistribution after collisions. Such trends turn out not to change much over the examined range of temperatures.

By looking at the results given in Fig. 10, we realize that to have either para- H_2 or ortho- H_2 as a collision partner changes the size of the involved rates only marginally. They turn out,

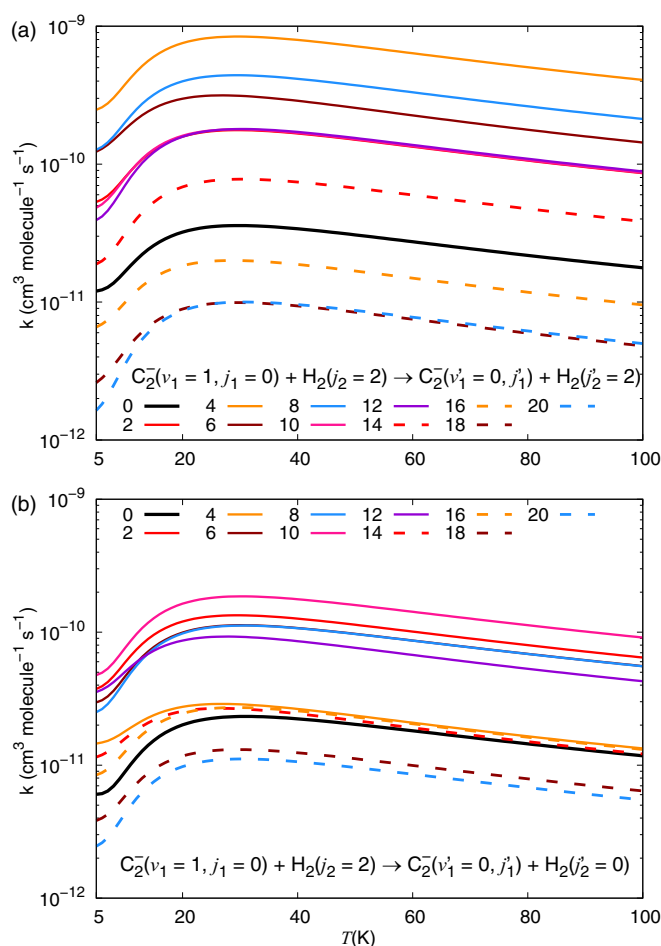


FIG. 11. (a) Plot of the (5D) computed rate coefficients for inelastic processes involving the molecular anion, with the rotational states changing up to $j'_1 = 20$, while the para- H_2 partner remains excited in its $j_2 = 2$ rotational state. (b) Same processes as in (a) but including the rotational deexcitation of the para- H_2 partner. See the text for further details.

however, to be close to each other at the lowest collision energies, with the ortho results becoming somewhat smaller as the collision energy increases. On the whole, however, we see a rather minor effect coming from either nuclear spin arrangement as a collision partner.

The calculated rate coefficients shown in Figs. 11 and 12 are considering more complex situations whereby the excitation of rotations involves not only the anionic partner but also either the para- H_2 or the ortho- H_2 molecular rotor. Such analysis will allow us to evaluate the relative energy-transfer efficiencies between the two partners when both undergo rotational state changes during the collision, the latter being chiefly driven by the vibrational cooling of the C_2^- partner. Only collisions using the 5D quantum dynamics are shown in Figs. 11 and 12.

Figure 11(a) shows rotational excitations of rotor states of the C_2^- partner from $j'_1 = 0$ up to $j'_1 = 20$, with the para- H_2 partner in its excited $j_2 = 2$. The relative probabilities for the various excitation processes are clearly changing when the para- H_2 partner is excited and turn out to be markedly larger than those obtained with the partner molecule is in its ground

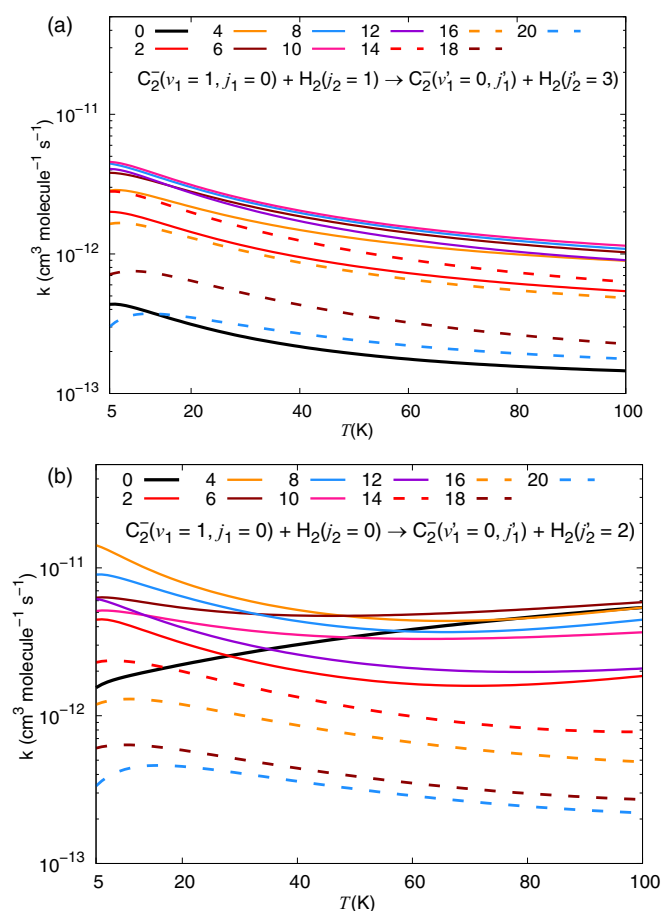


FIG. 12. (a) Plot of the (5D) computed rate coefficients for inelastic processes involving the molecular anion with the concurrent rotational excitation of the ortho- H_2 as a partner. (b) Same processes as in (a) but including the rotational excitation of the para- H_2 partner. See the text for further details.

rotational state [Fig. 11(a)]. On the other hand, the results in Fig. 11(b) indicate that the concurrent deexcitation of the para- H_2 partner causes all transition probabilities to become somewhat smaller, although still larger than those given in Fig. 11(a). We see once more that the size of the various processes is largely controlled by the dominant size of the initial vibrational deexcitation process, so all rate coefficients never get larger than about $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at the most, while being largely around $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

In Fig. 12 we further present the cases of rotational excitation of the various states of C_2^- up to $j'_1 = 20$, with the concurrent excitations of either the ortho- H_2 partner [Fig. 12(a)] or the para- H_2 partner [Fig. 12(b)]. We clearly see from the data of both panels that involving the much larger energy of the H_2 rotors generates rate coefficients which are smaller than in the case where only the anionic partner undergoes rotational excitation (see Fig. 12). In the lower-temperature range, in fact, their sizes are down by nearly one or two orders of magnitude with respect to those in Fig. 12 and remain so even at the highest-temperature values we consider. This feature of the rate coefficient behavior will be further analyzed below.

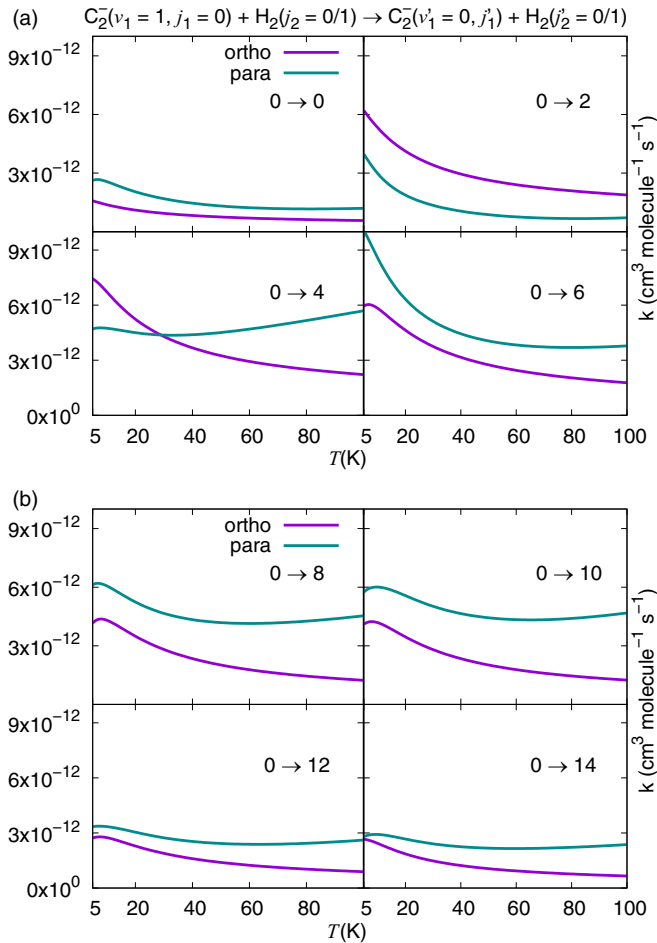


FIG. 13. Plot of the (5D) computed rate coefficients for inelastic processes involving the molecular anion colliding with either the ortho-H₂ or the para-H₂ partner in their ground rotational states. The different panels indicate different rotational states of the anion which are being populated during each collision process. See the text for further details.

An additional comparison of the various rotational final states of the anion which become populated during the vibrational cooling process is given by the data of Fig. 13. We indicate there the cases where the neutral molecular partner is always in its ground rotational state and is given by either the para-H₂ (green lines) or the ortho-H₂ (purple lines). The various panels further report, as before, different final rotational states of the anion being populated during the collisions. We can make the following comments about the data shown in Figs. 13(a) and 13(b).

(i) For the purely vibrational deexcitation process [shown in the topmost left panel in Fig. 13(a)] we see that the rates

$$k_{v \rightarrow v'}(T) = \frac{1}{\sum_{j_1} (2j_1 + 1) \exp[-(\epsilon_{vj} - \epsilon_{v=0j_1=0})/k_B T]} \left(\sum_{j_1} (2j_1 + 1) \exp[-(\epsilon_{vj} - \epsilon_{v=0j_1=0})/k_B T] \sum_{j'_1} k_{vj \rightarrow v'=0j'_1}(T) \right).$$

To simplify the notation in this equation we have replaced the subscript (v, j_1, j_2) with the simpler form (v, j) .

with the para-H₂ partner are larger over the whole temperature range considered.

(ii) When the lower rotational states of the anion are also populated [Fig. 13(a)] we see that the ortho rate coefficients are larger only for the case where the $0 \rightarrow 2$ rotational excitation process occurs, while they constantly remaining smaller by varying factors between 2 and 5 over the results of also Fig. 13(b).

(iii) We can therefore say that the present calculations involving state-to-state transitions of the rovibrational states of the anion yield smaller probabilities at the temperature of interest when the ortho-H₂ is considered as a collision partner.

Such findings are expected to produce significant differences when comparing the present calculations with existing experiments, as we do in the following section.

Additional information and detailed numerical data regarding all computed rate coefficients are given in the Supplemental Material in Ref. [63].

C. Comparison of the 5D computed rate coefficients with the available experimental results

Since we wish to further compare the five-dimensional vibrational quenching rate coefficients calculated in the present work to those obtained in the experiments, we have to look more closely at the conditions in which observations were made in our earlier work of Ref. [52].

First of all, following the information from the experimental conditions, we assume that the excited vibrational state with $v = 1$ of the ground electronic state of C₂⁻, which has been prepared by laser cycles via the excited electronic states (as described in the Introduction), reaches a Boltzmann distribution for the initial rotational states at the temperature of the trap conditions. This is justified by the fact that rotational quenching is known to be far faster than vibrational quenching, so we can learn from experiments which rotational states of the initial vibrationally excited anion will be populated during the ensuing collisional quenching step; however, we cannot say which will be the populated rotational states of the quenched anion after collision.

The observable vibrational quenching rate constant $k_{v \rightarrow v'}(T)$ could thus be modeled from our calculations by summing over all final rotational states, reached after the cooling down of the C₂⁻ to the $v = 0$ state by collision, for which we find the quenching rate coefficients to be significant in size. On the other hand, we are able to carry out a Boltzmann averaging over all the initial rotational states of the anion, in the $v = 1$ state, which are known to be populated before the collisional quenching. The temperature of the latter set of C₂⁻ molecules was considered in the experiments of [52] to be close to 20 K. Hence, we can write

We actually have covered a broader range of temperatures of interest (5–100 K) in our calculations. As discussed

in previous sections, we have treated the C_2^- anion as a pseudosinglet since we have verified in many earlier studies (see, e.g., [51] and references cited therein) that the effect of actually including the fine-structure terms alters the final cross-section values by less than a few percent. We also know that only the first few rotational states are significantly populated at the temperature of the experiment carried out, e.g., $j_1 = 0-4$, and so only these were used as starting j_1 states. On the other hand, all the final j'_1 states used in our basis set, and producing significant rate coefficient values, went up to $j'_1 = 20$, so all the calculations into those final states were used in the sum indicated in Eq. (16).

It is instructive at this point to pictorially verify the relative size distributions of the final states ending up with $v = 0$, but with different j'_1 , by looking at a bar spectrum representation of the computed data. Figure 14 plots such data for three different temperature values and for three different choices of j_1 when the anions are in the $v = 1$ state before the collisional quenching of the vibration. Only the case where the para- H_2 is considered as a collision partner are shown in that figure.

The following observations could be made when looking at the rate coefficient distributions shown in the various panels of Fig. 14.

(i) When the initial rotational state $j_1 = 0$ the probability of transferring energy into excited rotational states peaks at $j'_1 = 6$ for all temperatures, with the rate coefficients for $j'_1 = 8$ and 10 also being significantly large. The higher final states exhibit successively smaller probabilities of occurrence.

(ii) When the initial states are either $j_1 = 2$ or 4, the largest rotational energy transfers are seen for $j'_1 = 10$, hence showing a similar tendency to the previous case.

(iii) All the final rate coefficient values within each distribution consistently show that they become smaller when the initial state is $j_1 = 4$.

(iv) In addition, we see from all the data in Fig. 14 that the general trend as the final rotational state becomes larger is that the corresponding rate coefficients get larger, but up to a maximum j'_1 , after which the rate coefficients become smaller. These findings confirm that the quantum dynamics of angular momentum transfer probabilities gets increasingly less efficient when larger angular momentum changes occur during the collision, while also indicating that the smaller values of the rate coefficient pertain to the final states with $j'_1 = 0$.

The above findings certainly bear importance when we analyze the existing experimental datum taken from [52] and reported with the present computed findings by the curves given in Fig. 15.

The results of our present calculations, shown by the curves in Fig. 15, are now modeling the expected distributions into the final rotational states of the collisionally cooled anion, as already discussed in the previous paragraphs. More specifically, the red curve there presents the averaged rate coefficients obtained following Eq. (16) and involving the concurrent rotational excitation of the para- H_2 partner, while the purple curve shows the same calculations from Eq. (16) but only involves the population of the rotational states of the anion. The next two (brown and blue) solid curves show the same processes given by the two upper curves but dealing

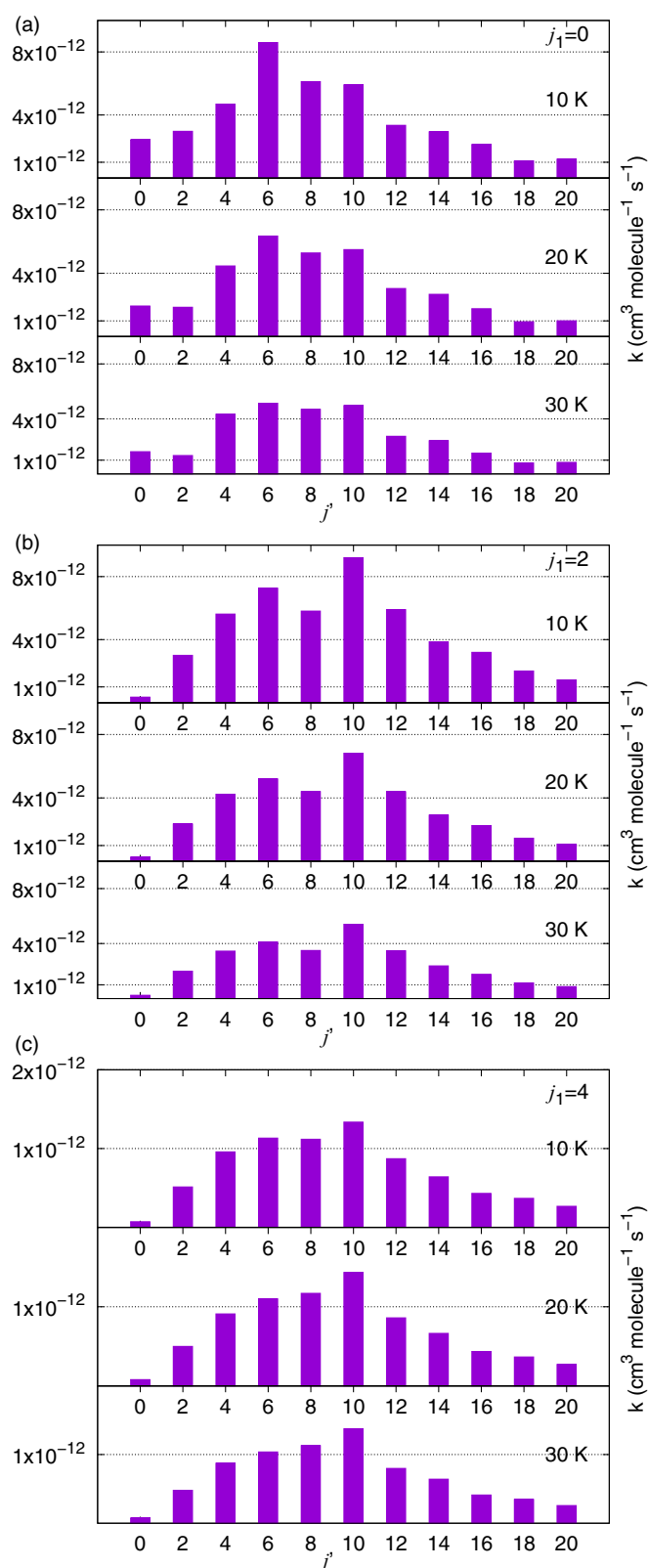


FIG. 14. Computed rate coefficient distributions over the final rotational state after collisional cooling of the anion with para- H_2 ($j_2 = 0$) as a partner. The data are presented as vertical bars for each final rotational state. The initial state before the vibrational cooling changes in each set of panels: (a) the initial state $j_1 = 0$, (b) the initial state $j_1 = 2$, and (c) the initial state $j_1 = 4$. Three different temperatures are shown in each panel. See the text for further details.

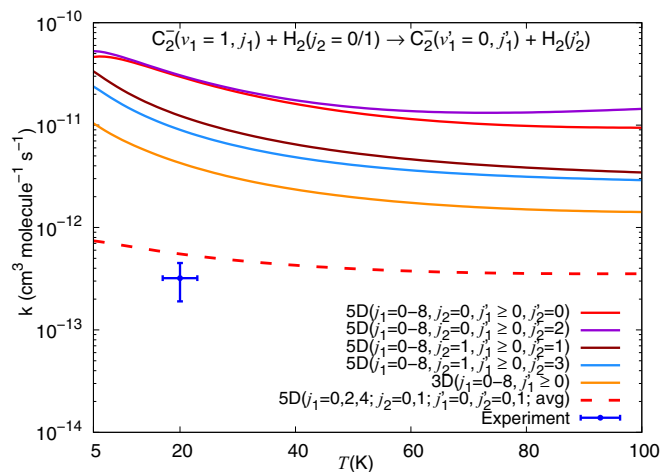


FIG. 15. Computed rate coefficients for vibrational deexcitation for the anionic partner with all the rotationally inelastic processes Boltzmann averaged at $T = 5$ – 100 K. See the text for details. The (top) purple curve refers to the 5D dynamics where the para- H_2 partner is also rotationally excited from its ground state to the $j'_2 = 2$ state, while the red curve involves only rotational states of the anion. The next two curves (brown and blue) describe the same set of processes but this time having ortho- H_2 as a partner. The lower yellow curve represents data like the previous red curve, but this time obtained using the 3D dynamics reported in our earlier work [52]. All the initial states used to obtain these curves have been thermally averaged over rotational (from 0 to 8) initial states according to Eq. (16). The red dashed curve shows rate coefficient values obtained by averaging the dominant first three initial j_1 states with the experimental distribution at 20 K but including only the final rotational state with $j'_1 = 0$. It is further obtained by the weighted sum of $3/4 + 1/4$ of the results involving either the ortho- or the para- H_2 collision partner. The single blue point corresponds to the only available experimental observation from Ref. [52].

with the ortho- H_2 as a partner; they clearly show that the rate coefficients linked to the ortho- H_2 as a partner are smaller than when the collision partner is the para- H_2 molecule. The slightly lower yellow curve presents the earlier 3D calculations of our earlier work [52], where only excitation of the anion's rotations were considered in the inelastic process and the para- H_2 was the only possible collision partner, as we have discussed in the earlier sections.

The only existent experimental point, estimated to be at 20 K, is given in Fig. 15 by the blue cross and taken from [52]. It indicates that all full 5D calculations yield invariably larger rate coefficients than the one given by the experiment, even when the excitation of either the para- or the ortho- H_2 partner is included in the quantum dynamics. The calculations where the more realistic 5D PES is employed within the quantum dynamics invariably yield larger values which are nearly two orders of magnitude larger than the available experimental point.

To possibly better understand the findings of the present comparison, we have included in Fig. 15 an additional set of results, given by the red dashed curve. The red dashed curve represents purely vibrational cooling, starting from the thermal averaging of the three dominant rotational states of the initial anion before the collisional cooling: $j_1 = 0, 2$, and 4

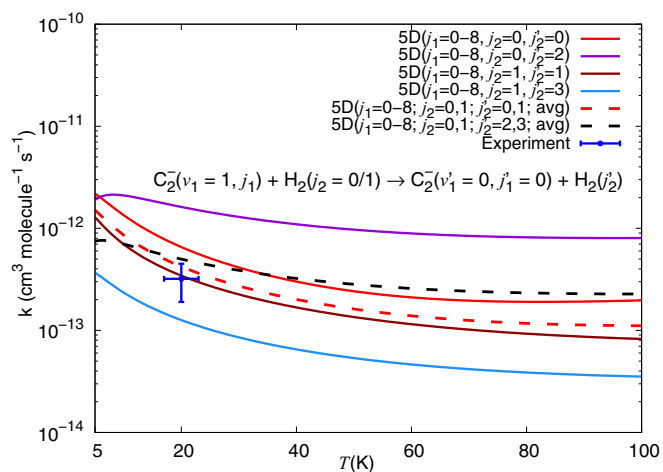


FIG. 16. Computed rate coefficients for vibrational deexcitation for the anionic partner with all the rotationally inelastic processes Boltzmann averaged at $T = 5$ – 100 K (see the text for details). The purple curve refers to the 5D dynamics where the para- H_2 partner is rotationally excited from its ground state ($j_2 = 0$) to the $j'_2 = 2$ state, while the light blue curve refers to the ortho- H_2 partner getting excited from the $j_2 = 1$ state to the $j'_2 = 3$ state. Thus, the red and brown curves involve only rotational states of the anion, while the purple and light blue curves show the cases where either the para- H_2 or the ortho- H_2 partner is rotationally excited. All the initial states used to obtain these curves have been thermally averaged over $j_1 = 0$ – 8 initial states according to Eq. (16) while the final rotational state of the anion was selected to always be the $j_1 = 0$ state. The red and black dashed curves show rate coefficient values obtained by averaging the dominant first three initial j_1 states with the experimental distribution at 20 K and further obtained by the weighted sum of $3/4 + 1/4$ of the results involving either the ortho- or the para- H_2 collision partner. In the case of the red dashed line the H_2 partners are kept in their ground rotational states, while the black dashed curve involves both ortho and para partners in their rotationally excited states.

at 20 K. On the other hand, only the final, vibrationally cooled anionic states with $j'_1 = 0$ are considered. The calculations are those obtained using the present extended surface in five dimensions and only for that single process. Furthermore, we have considered the role of either the para- or the ortho- H_2 partner in collision with the present anion and have included in the data shown by the red dashed curve a weighted sum of $1/4 + 3/4$ of the two sets of processes.

We see now that the purely vibrationally inelastic processes which occur without formation of rotationally excited anions in the $\nu = 0$ state get markedly closer to the existing experimental point. The efficiency of the 5D calculations, at the experimental temperature of about 20 K, makes the initially averaged 5D calculations to be about $5.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, to be compared with an experimental value of about $4.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Such results are clearly very close to each other.

Another interesting effect is provided by the analysis of the size and behavior of the inelastic rate coefficients shown by Fig. 15 when we separately analyze the collision results dealing with either the ortho- H_2 or the para- H_2 partner of the

main anion. This analysis is shown by the data in Fig. 16. These data clearly indicate the following features.

(i) Rotational excitation in the para- H_2 partner produces by far the largest vibrational cooling rate coefficients.

(ii) In contrast, rotational excitation in ortho- H_2 as a collision partner leads to the smallest vibrational cooling rates, well below the experimental finding.

(iii) The presence of either pure ortho- or pure para- H_2 partners (red and brown curves) without them being excited has a much smaller effect on the vibrational cooling rates.

(iv) However, when one considers the relative weights of the two species in normal- H_2 (red and black dashed curves) we see that the difference in cooling efficiency becomes again rather small and the two dashed curves are close to the experimental value.

There are two different aspects of these findings that require explanation: (i) why smaller energy transfers are yielding larger rate coefficients and (ii) why limiting the final states to the pure vibrational cooling is bringing our calculations closer to the experimental data. As for the first point, we already know that quantum dynamics yields in general larger probabilities for a final state to be reached whenever this event results in a smaller amount of energy being transferred. Hence, the production of a series of final anions which still retain some of their internal rotational energy is expected to happen with larger rate coefficients than when the amount of energy being transferred is larger, as when no internal energy is present in the final anion's rotational states.

However, explaining why this expected behavior brings our calculations closer to the experimental finding is still an open question, one which would imply that the energy redistribution in the experiments dramatically favors final states of the anion where no internal energy is left in their rotational states. Such behavior is however unphysical in terms of what is meant to occur under the experimental conditions.

It is also interesting to note, as an aside, that the rate coefficients for vibrational cooling occurring among the same levels of the present anion become dramatically smaller when He is used as a collision partner instead of H_2 . For example, the cooling rate at 100 K, taken from our earlier work of Ref. [51], is about five orders of magnitude smaller than the one we found here for the H_2 partner.

D. Testing the numerical stability of the computed results

Although the full sequence of the present computational modeling has been carried out using exact theoretical methods and converged numerical procedures, it is still useful to further analyze the results by checking separately the steps of the full sequence to see how much the results of each step would change when more extended, albeit equivalent, numerical expansions are employed.

To this end, for example, the accuracy of the computed *ab initio* values of the 5D PES is tested by selecting a specific orientation and then generating all the points again using different basis set expansions. More specifically, we employ in sequence the aug-cc-pVTZ (AVTZ), aug-cc-pVQZ (AVQZ), and aug-cc-pV5Z (AV5Z) basis set expansions, bearing in mind that the complete set of calculations for the present paper use the AVQZ basis set expansion. We also correct our results

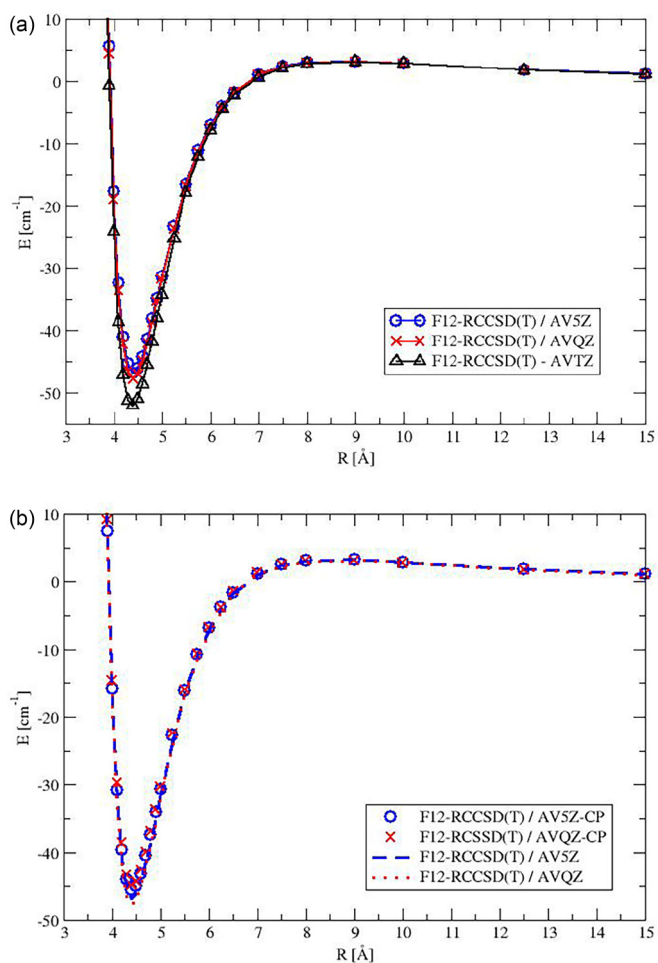


FIG. 17. Comparison of computed *ab initio* potential energy values using different basis set expansions. (a) Changes in the potential energy values with a change in the basis set size, indicated in the legend. (b) Shown for greater clarity is the effect of adding CP or BSSE corrections [68] for two of the basis set expansions employed. See the text for further details.

for the basis set superposition error (BSSE) [68], as explained below. More specifically, Fig. 17(a) shows the different potential energy curves as a function of R , obtained by using different basis sets for the geometry in which both molecules are frozen at their equilibrium bond lengths. The distance between the two molecules is then varied and H_2 approaches C_2^- along the CC axis and rotates 90° with respect to this axis. The radial distance in the plot is the distance between the two molecular centers of mass. The energies are set to zero at $R = 25 \text{\AA}$. We clearly see from the different potential energy curves that the results obtained using the aug-cc-pVQZ and aug-cc-pV5Z basis sets do not differ by more than a few cm^{-1} along the entire radial range examined.

For greater clarity, Fig. 17(b) shows the results obtained by using the AVQZ and AV5Z basis sets with BSSE or counterpoise (CP) [68] correction. The CP corrected results differ from the uncorrected results only by a couple of cm^{-1} near the potential energy minimum of the order of 45 cm^{-1} . We therefore conclude that the CP (or BSSE) corrections [68] play only a marginal role in deciding the potential energy surface for the present system.

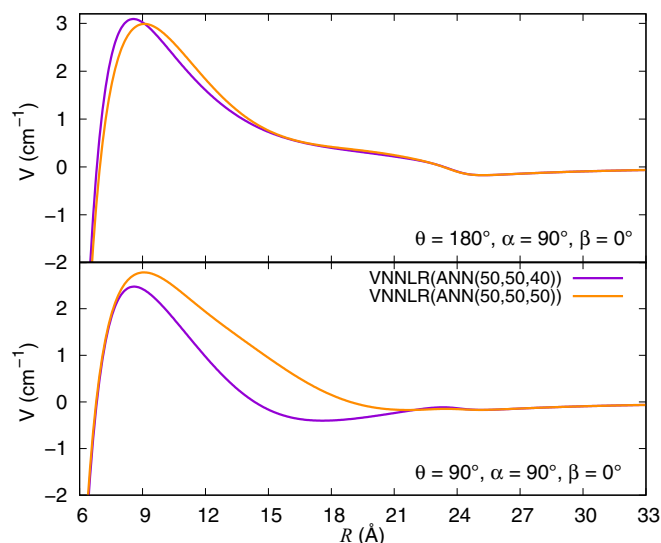


FIG. 18. Computed behavior of the ANN fitted interaction potential for different choice of nodes shown for the same specific geometries reported earlier in Fig. 4.

The next item within the sequence of numerical tests undertaken is the difference in the number of nodes used in the ANN fitting procedure discussed earlier in Sec. II A: (50,50,50) versus (50,50,40). The results reported in Fig. 18 demonstrate clearly that the two ANN fitted potential energy values are close to each other over the entire range of R for the two test geometries, hence confirming the robustness of the present numerical procedure. In the next step of the present tests on the numerical stability of the different parts of the computational modeling of the present work, we compute the inelastic cross sections for two different initial conditions using the ANN (50,50,40) fitted potential and compare them with the results presented earlier using the ANN (50,50,50) fit in Sec. IV A. The results presented in Fig. 19 show a variety of comparisons, with the earlier calculations represented by the green lines. The results from the present work, obtained using the ANN (50,50,40) fit, are represented by the purple curves. The comparisons, reported for different transitions and for different states of the neutral partner molecule, clearly indicate limited changes occurring between the two sets of curves, a harbinger of fairly small modifications to be expected in the final inelastic rate coefficients.

It is also interesting, for the present testing of the sensitivity of our calculated quantities to the numerical accuracy of different steps, to view once more the direct vibrational coupling matrix elements shown as radial coefficients in Fig. 5 discussed earlier. The comparison is shown in Fig. 20. Figure 20(a) compares the three lower expansion coefficients for the diagonal coupling term as given in Fig. 5 (green lines) with their more recent evaluation using the ANN (50,50,40) fitting procedure (purple curves). We clearly see that the coupling terms hardly change when a slightly different ANN fitting procedure is employed. The same types of matrix elements are shown in Fig. 20(b), where the off-diagonal (0-1) vibrational coupling coefficients are shown. Once again, we see that the two sets of curves (purple and green) are nearly indistinguishable in spite of the different ANN fits used. It

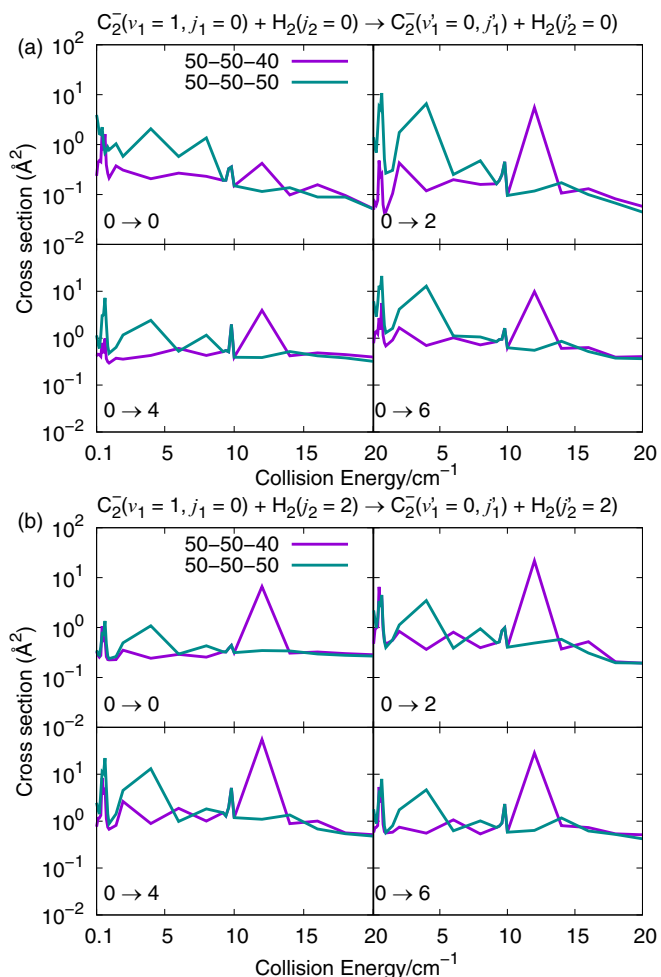


FIG. 19. Comparison of computed inelastic cross sections using the two different ANN fits for two examples of the many vibrationally inelastic processes considered in this work. The neutral partner is always in its (a) ground rotational state and (b) $j = 2$ rotational state. The green curves are the results of the earlier calculations, while the purple curves present the results from the present work. See the text for further details.

is clear that the present treatment is indeed stable and nearly unchanged by changes in the fitting parameters (nodes).

It is also worth noting at this point that the off-diagonal coupling terms act over a rather short range of relative distances between partners, becoming essentially negligible beyond about 5.0 Å. This is in keeping with the previous discussion of the vibrational coupling dynamics reported earlier.

The final test of the changes of our dynamical observables against fitting modifications is clearly given by direct comparisons between the inelastic rate coefficients, as presented in Fig. 21. Figure 21(a) compares vibrational relaxation rate coefficients involving only the vibrational and rotational levels of the anion, while the H_2 partner remains unchanged in its ground rotational state. The case in which the neutral partner is also rotationally excited is in Fig. 21(b).

Figure 21(a) confirms the low sensitivity of the final inelastic rate coefficients to changes in the ANN fitting procedure: The purple and green curves are always very close to each other and indicate strong numerical stability of the present

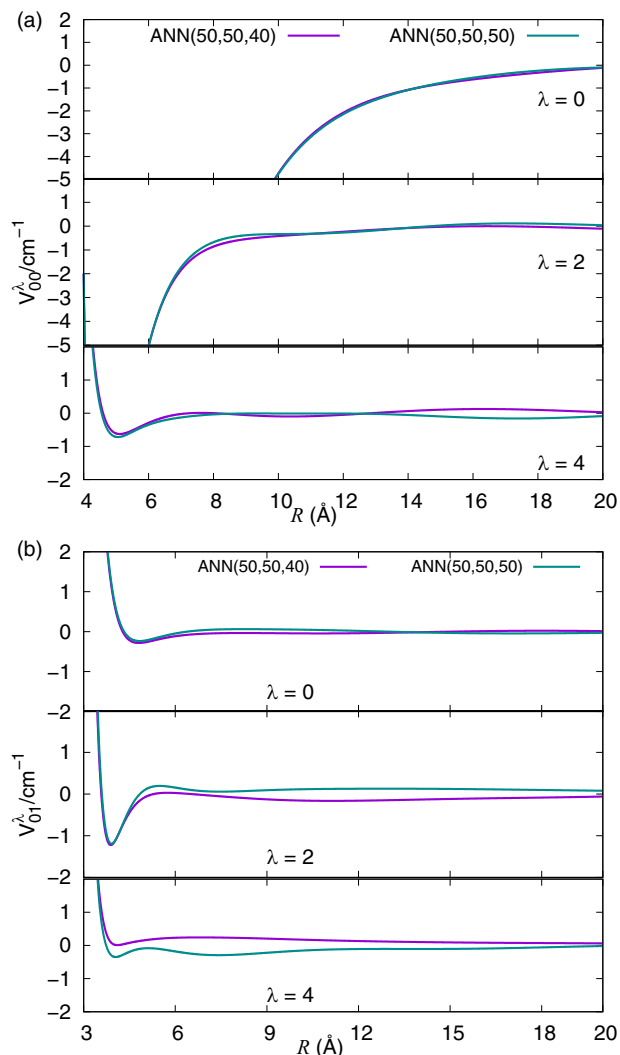


FIG. 20. Comparison of the computed vibrational coupling potentials obtained using the ANN (50,50,50) and ANN (50,50,40) fits. See the text for further details.

calculations. The same is true of Fig. 21(b), although in this case minor departures in relative size are seen between the purple and green curves. We should also note that, in the fit (50,50,40) for rate calculation, we used 25 energy points in the range from 0.1 to 20 cm^{-1} and used the same energy points in the (50,50,50) calculations. We can therefore conclude from the results of this section that the computed inelastic rate coefficients discussed in the present work are stable against changes in the basis set used in the *ab initio* calculations and in the number of nodes used in the ANN fit of the *ab initio* potential.

V. CONCLUSION

In the present work we have analyzed in detail the quantum dynamics of an ion-neutral system, the ground electronic state of the C_2^- interacting with the corresponding ground electronic state of the neutral H_2 molecule. More specifically, we have carried out detailed calculations for the dynamics of the vibrational cooling of the anion in collision with the

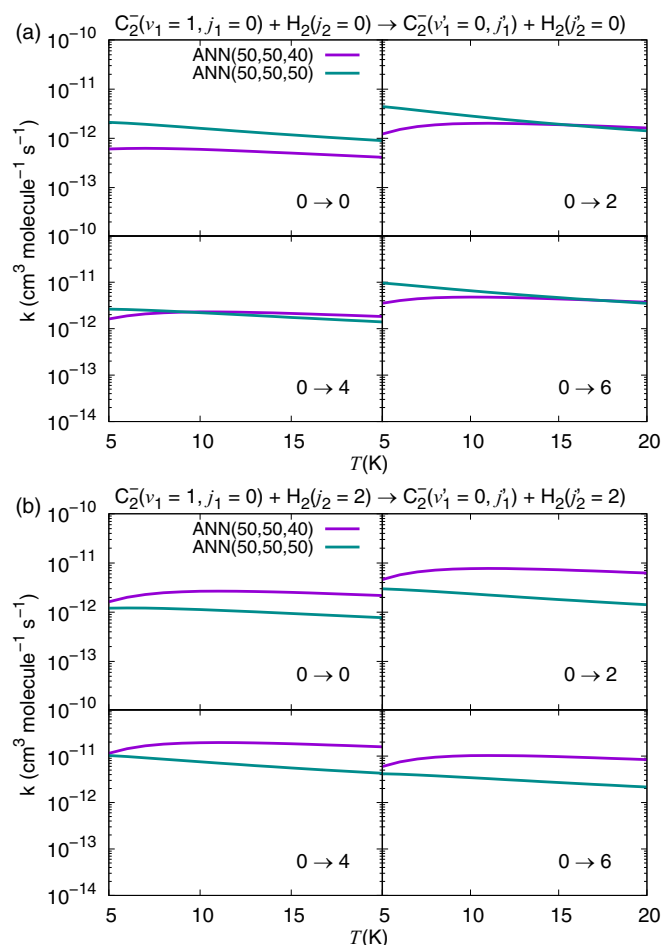


FIG. 21. Comparison of computed inelastic rate coefficients for two examples of the vibrational inelastic processes we consider in this work, involving the neutral partner always in its (a) ground rotational state and (b) $j = 2$ rotational state. The green curves are the results of earlier calculations, while the purple curves shows the results of the present work. See the text for further details.

hydrogen molecular partner. The general conditions of the overall system we have studied were linked to low-temperature experiments done in our laboratory by injecting the two molecular partners in a cold ion trap, as described in more detail in one of our earlier papers, e.g., in [52]. We have also analyzed in great detail the complex dynamics of energy redistribution after collisions under low-temperature conditions exhibited by the present system.

By using accurate *ab initio* calculations we have obtained a large grid of points involving five dimensions for the process at hand: rotations of both the anion and the neutral molecule and vibrations for the anion during the interaction with the H_2 partner. Such a PES was meant to improve on our earlier studies of the same system, when the H_2 presence was accounted for via an averaged potential for the neutral partner, thus using a 3D PES to treat the same dynamics (see [52] for further details).

The main cooling process that we have considered here is the vibrational transition from $\nu = 1$ to $\nu = 0$ of the anionic partner, together with a wide range of concurrent

final populations of rotational states of the molecular ion in its ground vibrational state $\nu = 0$. The H_2 partner was considered to be a mixture of ortho and para states, as occurring in the experiment, and examples were considered in the calculations where the neutral molecule (*p*- or *o*- H_2) was rotationally excited to either its $j_2 = 2$ or 3 rotational state.

Several interesting features of the energy-transfer dynamics involving either the vibration or the rotations, or both of them, have been obtained from the present quantum dynamics, which is essentially an exact dynamics using the multichannel CC approach, as described in Sec. III.

(i) Both the state-to-state cross sections and the corresponding rate coefficients turn out to be larger when the final, vibrationally cooled, state of the anion was obtained in a variety of its excited rotational states. In other words, we found that the purely vibrational energy transfer, yielding the largest energy gap between the involved states, was occurring with the smallest rate coefficients while the concurrent rotational energy-transfer paths produced larger rates, up to fairly large transfers of rotation angular momentum. This type of behavior was found to occur for both para- and ortho- H_2 as collision partners.

(ii) The efficiency of energy-transfer processes by collision turned out to be larger for the para- H_2 partner, especially for transitions involving vibrational energy transfers. The present results are thus several orders of magnitude larger than in the case of inelastic rates computed when He or even Ar atoms are the collision partners, a result clearly in agreement with our earlier calculations of Ref. [51].

(iii) Our calculations also reveal that employing the more realistic 5D version of the interaction forces, i.e., one where the H_2 molecular partner is considered also a rotating molecule, in comparison with the simpler 3D version of our earlier work in [52] where the hydrogen molecule was treated as a structureless partner, yields invariably larger inelastic rate coefficients (see the comparison in Fig. 9). All the rate coefficients computed herein are seen in fact to be larger by varying amounts which are within about one order of magnitude of each other. In other words, the presence of a better description of the interacting systems causes the energy-transfer efficiency to the anionic partner by collision to uniformly increase for all processes.

(iv) When comparing the behavior of the neutral collision partners, i.e., ortho- H_2 and para- H_2 , we found in our calculations, as described, for example, by the data in Fig. 13, that considering the ortho- H_2 as the collision partner turns out to consistently yield smaller collision rates for all the cases examined in the present study.

The present calculations further indicate that obtaining the final anion in its ground vibrational state, but also in a variety of excited rotational states, yields rate coefficients which are uniformly larger than when no rotational energy is being stored in the cooled-down molecular anion. To be more specific, the data reported in Fig. 15 make a direct comparison with the only available experimental point, taken around 20 K. They show that our essentially exact calculations are about one or two orders of magnitude larger than the

measured datum when one factors into the modeling that the vibrational cooling via collisions occurs when the available internal energy is allowed to flow into a variety of excited rotational states of the final anions produced in the trap. On the other hand, only when the vibrationally cooled molecules are allowed to also reach their ground rotational state after the collisional process (which is deemed to be a nonphysical option), hence producing anions with no internal energy content, we find that our modeling of the events gets very close to the order of magnitude of the experimental findings.

Quantum inelastic dynamics already tell us that those processes which involve the least amount of energy being transferred during a collision are occurring with larger probabilities; hence the differences in size between the top four curves and the dashed curve in Fig. 15 are in accord with such a general behavior. On the other hand, finding that such a decay option actually induces better agreement with the existing experiments is still an unexpected result, one that needs further investigation of the energy-transfer dynamics in this specific system. The calculations presented in this work are indeed accurately detailing the quantum dynamics of the investigated processes and able to clarify several aspects of the rovibrational inelastic collisions involving the two title molecules. Basically we have found that once the correct 5D interaction is considered and exact quantum dynamics cross sections are obtained, the spin condition of the H_2 partner plays an important role in the vibrational cooling efficiency. This is an unexpected result, which should be very useful in planning future cooling cycles of molecular anions.

We should also note that we have tested the sensitivity of our calculations against modifications of the numerical convergence parameters, as presented in detail by the results of Sec. IV D, and found very clearly that our final results have reached numerical convergence and are hardly changed by further modifications of the numerical parameters.

See Ref. [63] for the numerical data pertaining to our parametric fitting of the computed PES and to the actual values of the computed cross sections and rate coefficients for the inelastic processes discussed in the present paper.

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