Molecular vibration in cold-collision theory

Alessandro Volpi and John L. Bohn*
JILA and Department of Physics, University of Colorado, Boulder, Colorado 80309-0440
(Received 13 February 2002; published 5 June 2002)

Cold collisions of ground-state oxygen molecules with helium have been investigated in a wide range of cold-collision energies (from 1 μK up to 10 K) treating the oxygen molecule first as a rigid rotor and then introducing the vibrational degree of freedom. The comparison between the two models shows that at low energies the rigid-rotor approximation is very accurate and able to describe all the dynamical features of the system. The comparison between the two models has also been extended to cases where the interaction potential He-O_2 is made artificially stronger. In this case vibration can perturb rate constants, but fine tuning the rigid-rotor potential can alleviate the discrepancies between the two models.

DOI: 10.1103/PhysRevA.65.064702 PACS number(s): 34.20.Cf, 34.50.−s, 05.30.Fk

A wide variety of techniques is now available for the production of ultracold molecular gases, and collisions often play a crucial role in their success. The challenge for theoreticians is then a detailed understanding of the scattering properties at low temperatures, in order to assess the feasibility of the experiments. In this paper, our aim is to investigate the role of molecular vibration in cold collisions, a topic that has already been an object of interest, for instance, in the case of molecules produced by photoassociation (PA) [1–4]. This technique exploits one or more PA lasers to catalyze alkali atom pairs into bound molecular states [5], resulting in molecules with nearly the same translational temperature as the original atomic sample ($\sim$100 nK in the case of extraction from a Bose-Einstein condensate [4]). Although rotationally cold, these molecules are typically formed in high vibrational states, from which they can relax by collisions with another free atom. The understanding and characterization of this relaxation process is crucial, because a large amount of energy is released in the process, and this quenching can dramatically affect the efficiency of the cooling [6]. A study in this sense has been conducted for the He-O_2 system [7], pointing out the importance of understanding the role of vibration in ultracold molecular collision.

The buffer-gas cooling (BGC) technique [8,9], in which molecules are cooled by collisions with a cold buffer gas, also demands a detailed picture of the collisions. The lowest temperature reached so far is 0.3 K in a gas of CaH molecules, a result achieved by Weinstein *et al.* [10] who used the same technique recently to cool PbO molecules [11]. Appealing candidates for BGC would be O_2 molecules, already investigated from the theoretical point of view [12–14], and NH, for which, in addition, magnetic trapping has been proposed recently by the alternative Stark slowing technique [15].

Lower temperatures can be achieved via evaporative cooling, in which high-energy molecules are selectively removed from the trap. The success of the cooling requires that elastic rethermalizing collisions be much more efficient than the spin-changing process that produces untrapped molecules. Since several of our previous papers have demonstrated that spin orientations can be easily changed in cold molecular collisions, an important question raised in this work is whether the vibrational motion can further encourage spins to flip, even in the ground vibrational state of the colliding molecule.

Following Refs. [13,14,16], we evaluate here the state-to-state rate constants for collisions of molecular oxygen ($^{17}O_2$ isotopomers) with ^{3}He atoms, using a recently published potential-energy surface (PES) [17]. We first treat O_2 as a rigid rotor, then we introduce the vibrational degree of freedom in order to assess the influence of the vibrational motion. Results can also be compared with a previous calculation [13] on the same system performed by one of the authors on a different PES [18] using a rigid-rotor model. We show how the rigid-rotor approximation holds quite well for this system, as expected. This is because the atom-molecule interaction is very weak compared to the O-O interaction, and the O_2 molecule is strongly bound and physically very similar to a rigid rotor.

Nevertheless, for stronger three-body interactions or for shallower diatomic potentials, the rigid-rotor model could be unrealistic in describing the dynamical features of the system. What might happen in such a case is as well a subject of this paper. To this end, we consider a set of artificial models, by increasing the atom-diatom interaction strength while preserving the natural O-O interaction. Thus at some point the He atom in the artificial model will gain sufficient kinetic energy during the collision to excite vibrations of the O_2 molecule. The effect of vibrational degrees of freedom is primarily to provide additional phase shifts, which may be ''mocked up'' by suitable adjustment to the short-range potentials. In addition, vibrational resonances are introduced, but these should be small in number as compared to rotational resonances.

Throughout this paper we report energies in units of Kelvin by dividing by the Boltzmann constant k_B. These units are related to the more familiar wave numbers via 1 K$=0.695$ cm^{-1}. Lengths are expressed in units of the Bohr radius a_0.

We will consider molecules consisting of two ^{17}O atoms, whose nuclear spin i is equal to 5/2. We assume that total spin $\mathbf{I}=\mathbf{i}_1+\mathbf{i}_2$ is conserved in the collision, implying that the even molecular rotational states N are separated from the odd

*Email address: bohn@murphy.colorado.edu

ones [19]. Following Refs. [13,14,16], we limit our discussions to the ''even-N'' manifold of molecular states. However, we have performed some sample calculation for the ''odd-N'' manifold, finding results consistent with the conclusions for the case of even N.

Including the $S=1$ electronic spin of O_2, at low energies the molecules have total spin $\mathbf{J}=\mathbf{N}+\mathbf{S}=1$. The Hamiltonian operator $\hat{\mathbf{H}}_{O_2}$ for molecular oxygen is given by

$$\hat{\mathbf{H}}_{O_2}=-\frac{\hbar^2}{2\mu_{O_2}}\left[\frac{d^2}{dr^2}-\frac{N(N+1)}{r^2}\right]+V(r)+\hat{\mathbf{H}}_{fs}, \qquad (1)$$

where μ_{O_2} is the O-O reduced mass and V is the atom-atom potential depending on the stretching coordinate r. We have taken the fine-structure Hamiltonian $\hat{\mathbf{H}}_{fs}$ from Ref. [20] disregarding the molecular hyperfine interaction and using the fine-structure parameters determined in Ref. [21] by microwave spectroscopy. We assume these parameters to be the same for the ground and excited vibrational states.

The Hamiltonian in Eq. (1) refers to the vibrating diatom model, and obvious simplifications lead it to the appropriate expression for the rigid rotor. We note here that the molecular rotational quantum number N is no longer strictly a good quantum number for the molecular states, because different values of N are coupled together by the fine-structure Hamiltonian $\hat{\mathbf{H}}_{fs}$ [see Eq. (A5) in Ref. [20]]. However, since the fine-structure coupling is small compared to the rotational separation, different N's are mixed only weakly, so we will continue to use N to label the true channels in what follows.

As in Ref. [13] we will focus our attention on the weak-field-seeking state $|NJM_J\rangle=|011\rangle$ of the molecule. We are concerned both with the elastic collisions that preserve this state, and with ''loss'' collisions that yield the untrapped states $|010\rangle$ and $|01-1\rangle$. The relevance of these collisions for ultracold molecular studies has already been discussed in Refs. [13,14,16].

Reference [13] provided the theoretical framework for atom-diatom scattering, along the lines of the model originally due to Arthurs and Dalgarno [22,23], and properly modified to incorporate the electronic spin of the oxygen molecule. Here we briefly recall some features needed to understand the present calculation, pointing out the differences between the rigid rotor and the vibrating diatom approaches. We compute rate constants in zero magnetic field, as we are interested primarily in the comparison of the rate constants between the two models. The study of molecular collisions in a magnetic field is, however, a central topic for trapping purposes, which we have discussed elsewhere [16].

After multiplying the wave function by R in order to remove first derivatives, the full Hamiltonian operator describing the He-O_2 collision is given by

$$\hat{\mathbf{H}}=-\frac{\hbar^2}{2\mu}\left[\frac{d^2}{dR^2}-\frac{\hat{\mathbf{L}}^2}{R^2}\right]+\hat{\mathbf{H}}_{O_2}+V'(R,r,\theta), \qquad (2)$$

where μ is the reduced mass for the He-O_2 system, R is the length of the Jacobi vector joining the atom to the molecule center of mass, $\hat{\mathbf{L}}^2$ is the centrifugal angular-momentum operator, and $\hat{\mathbf{H}}_{O_2}$ is the molecular oxygen Hamiltonian defined in Eq. (1). The potential term V', depending, in general, on R, r, and the bending angle θ that the molecule's axis makes with respect to $\mathbf{R}$, accounts for the He-O_2 interaction [17]. The O-O interatomic contribution is already included in the molecular Hamiltonian $\hat{\mathbf{H}}_{O_2}$. We note here that the PES considered in this work differs from the one by Cybulski *et al.* [18] used in a previous calculation by one of the authors [13]. In particular, the potential well for the three-body interaction is found to be about 30% deeper for the new PES with respect to the preceding one (however, the PES [18] was deepened by 20% in the calculations presented in Ref. [13]). The two potential surfaces provide consistent results: the s-wave scattering lengths are ~ -2.9 a.u. and ~ -1.5 a.u. using the PES [17] and [18], respectively.

If the rigid-rotor model is adopted, the internuclear distance r is frozen to its equilibrium value $r_0=2.282a_0$ and any dependence of the Hamiltonian on this coordinate is neglected. In this case, the theoretical formulation of the problem reduces to the one in Ref. [13], to which we refer for details. For the vibrating diatom, the r dependence of the Hamiltonian is taken into account.

The full multichannel calculation requires casting $V'(R,r,\theta)$ in an appropriate angular-momentum basis. Namely, we express the Hamiltonian in a basis of total angular momentum $\mathcal{J}=\mathbf{N}+\mathbf{S}+\mathbf{L}$, in terms of the molecule's mechanical rotation $\mathbf{N}$, its electronic spin $\mathbf{S}$, and the partial wave representing the rotation of the molecule and the He atom about their center of mass $\mathbf{L}$. Our basis for close-coupling calculations is then

$$|O_2(^3\Sigma_g^-)\rangle|\mathrm{He}(^1S)\rangle|vN[JL]\mathcal{J}M\rangle, \qquad (3)$$

where the electronic spin quantum number S is not explicitly indicated being always equal to 1 in the calculation presented here. Vibrational wave functions are computed for a particular value of N then transformed to the J basis. Evaluation of V' in the basis (3) has been discussed in Ref. [13]. As for the integration of the matrix elements over the vibrational coordinate r, we have performed numerical Gaussian quadratures.

Once the Hamiltonian is in place, the coupled-channel equations are solved subject to scattering boundary conditions to yield scattering matrices. Since we assume zero magnetic field the total angular momentum $\mathcal{J}$ is a good quantum number, and moreover the results are independent of the laboratory projection $\mathcal{M}$ of total angular momentum. In the context of magnetic trapping, the resulting total-$\mathcal{J}$ scattering matrices can be conveniently transformed to a basis labeling the magnetic quantum numbers, namely, $\langle vNJM_JLM_L|S|v'N'J'M'_JL'M'_L\rangle$. Note that, in general, all the quantum numbers v, N, J, M_J, L, and M_L are subject to change in a collision. However, at the energies we consider, only changes in M_J are energetically allowed. Cross sections and state-to-state rate coefficients are then obtained as in Ref. [13].

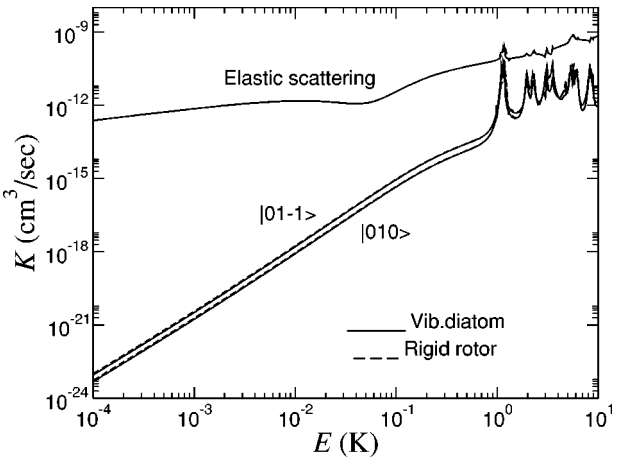

FIG. 1. Elastic and inelastic rate constants relative to the entrance channel $|NJM_J\rangle = |011\rangle$ in the 100 μK–10 K collision energy range. For each curve the final state is indicated. Solid and dashed lines refer to the vibrating diatom and rigid-rotor models, respectively: on this scale, the two models can barely be distinguished.

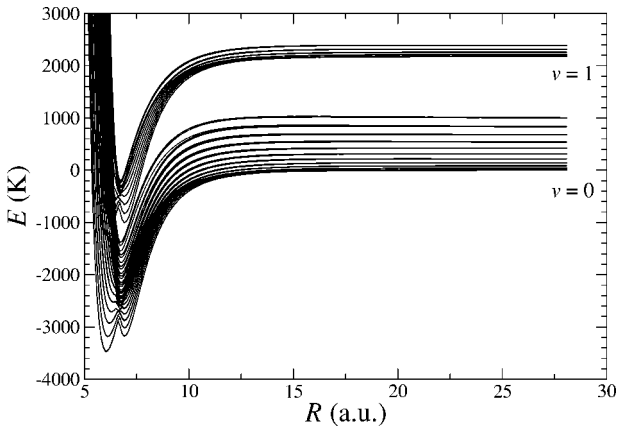

FIG. 2. Adiabatic curves for total angular momentum $\mathcal{J}=1$ when the He-O_2 interaction potential is boosted by a factor $\lambda = 90.5$. For this value of λ, the three-body well depth is larger than the vibrational excitation, leading to the possibility of new vibrational resonances. Not all the rotational states included in the calculation are shown here in order to preserve the clarity of the picture.

For ^{3}He-$^{17}O_2$ collisions, rate constants relative to the entrance channel $|NJM_J\rangle = |011\rangle$ for the elastic transition and the inelastic ones (to the states $|01-1\rangle$ and $|010\rangle$) have been calculated in a wide range of collision energy, from 1 μK up to 10 K, using both the rigid-rotor and the vibrating diatom model. We have found that rotational states up to $N = 8$ and partial waves up to $L = 8$ must be retained in the calculations. Scattering calculations are performed using a log-derivative propagator method [24] starting from $R = 4.1$ bohrs. We separate the propagation into two parts, from $R = 4.1$ to 24.0 bohrs, with a step size of 0.01 bohr, and then from $R = 24.0$ until the asymptotic limit of $R_{max} = 450$ bohr adopting a larger step size of 0.1 bohr. These parameters assure rate constants convergent within less than 1%.

We recall the rovibrational structure of the oxygen molecule. The zero-point energy is $\sim$1100 K above the bottom of the potential curve, and the vibrational separation between the ground and the first excited vibrational level is $\sim$2175 K. The rotational constant for the molecule is about 1.95 K. We have verified that the inclusion of the first rotational levels $(N = 0,2,4,6)$ of $v = 1$ modifies our results only within 0.5%.

Results are shown in Fig. 1 on a bilogarithmic scale. The two compared models provide nearly perfectly consistent results: the curves are virtually indistinguishable, results of the rigid rotor differing by at most 10% from the complete calculation that allows the O_2 molecule to vibrate. We have seen how these small discrepancies can be washed out by adjusting the short-range potential of the rigid-rotor Hamiltonian. This artificial ''fine tuning'' is already a common practice in cold-collision theory, as it enables both an accurate fit to experimental data, and predictive power [25]. Our results suggest that the main influence of vibration might be absorbed into a similar fine tuning, at least until high-resolution data are available that demand a more accurate model.

An exception occurs near a resonance, where the extreme sensitivity of phase shifts to details of the potential alters the line shape slightly. However, the overall agreement is quite good and demonstrates the adequacy of the rigid-rotor model in this case. The reason for this is obvious: the attractive well depth of the He-O_2 interaction is only $\sim$40 K, so that the incident He atom does not have nearly enough energy to excite vibration in the molecule, even as a virtual excitation. We expect this conclusion to hold generally in BGC, owing to the relatively weak interaction of Helium with anything, and also for O_2-O_2 cold collisions [14] since the intermolecular well depth is only $\sim$200 K. In this case in fact, the atom-atom exchange (which could be affected by vibration) is unlikely to take place, because at low temperatures the two oxygen molecules do not get close enough in the collision process.

For many systems this separation of the energy scales may no longer be the case, and vibrations may play a more important role. To study this influence, the He-O_2 interaction potential [V' in Eq. (2)] has been made artificially deeper by multiplying it by an arbitrary factor λ, ranging from 1 to 100. For $\lambda = 100$, the well depth of the three-body potential is approximately twice as large as the lowest vibrational excitation energy of O_2. We note here that increasing λ has two effects: first, it makes vibrational resonances energetically possible, and, second, introduces many more rotational resonances, since rotational energy splitting is much smaller than the vibrational one. This is made intuitively clear in Fig. 2, where a set of adiabatic potential curves for $\mathcal{J}=1$ are displayed for a large value of the factor λ.

We will refer in the following to very low collision energy (1 μK) because this allows us to include only total $\mathcal{J}=1$ in our calculations, thus reducing computational effort [16]. Figure 3 plots, both for rigid rotor and vibrating diatom, the elastic and total inelastic rate constants for the same transitions considered in Fig. 1 as a function of λ. As the potential is made deeper (larger λ), new He-O_2 bound states appear, which show up as resonancelike features in the figure. Two

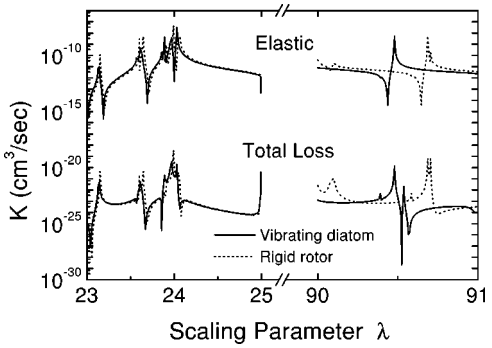

FIG. 3. Elastic and inelastic rate constants for the entrance channel $|011\rangle$ as a function of the scaling factor λ for collision energy $E=1$ μK. Solid and dashed lines refer to the vibrating diatom and rigid-rotor models, respectively.

different λ ranges are displayed, corresponding to two different physical situations. In one range ($\lambda=23$–25), vibrationally excited molecular states are not energetically accessible, whereas in the range 90–91 vibrational resonances are accessible. In the first case, the resonance pattern appears just a little shifted going from one model to the other, while in the second case, apart from a bigger shift, some different features are present in the rate constant trends.

However, the magnitudes and overall patterns of the rate constants are comparable in the two models. This suggests that, as for the original He-O_2 problem ($\lambda=1$), in modeling cold collisions the rigid-rotor Hamiltonian can be adjusted (by varying λ in this simple case) to nearly reproduce the results of the full vibrating case. We have indeed seen this in the energy dependence of the rate constants for several different λ values.

In conclusion, we find that the rigid-rotor model is very accurate for cold collisions of He with O_2. This has been proven for this system, but can be extended as well to stronger interaction potentials, as long as the energetic gain in the three-body interaction does not exceed the vibrational excitation energy. Even in this case, the discrepancies can be handled by fine tuning the interaction, at least until high-resolution data become available.

We notice that this is not true for interactions such as $A+A_2$, where A is, for example, an alkali atom. In such systems, moreover complicated by exchange effects between identical atoms, vibration can not be neglected *a priori*, not even for collision energies tending to zero.

This work was supported by the National Science Foundation and by NIST. A.V. acknowledges financial support from the Università degli Studi di Perugia (Italy).

[1] A. Fioretti *et al.*, Phys. Rev. Lett. **80**, 4402 (1998).
[2] T. Takekoshi, B.M. Patterson, and R.J. Knize, Phys. Rev. Lett. **81**, 5105 (1998); Phys. Rev. A **59**, R5 (1999).
[3] A.N. Nikolov *et al.*, Phys. Rev. Lett. **82**, 703 (1999).
[4] R. Wynar *et al.*, Science **287**, 1016 (2000).
[5] J. Weiner, V.S. Bagnato, S. Zilio, and P.S. Julienne, Rev. Mod. Phys. **71**, 1 (1999).
[6] N. Balakrishnan, R.C. Forrey, and A. Dalgarno, Phys. Rev. Lett. **80**, 3224 (1998); R.C. Forrey, V. Kharchenko, N. Balakrishnan, and A. Dalgarno, Phys. Rev. A **59**, 2146 (1999); R.C. Forrey *et al.*, Phys. Rev. Lett. **82**, 2657 (1999).
[7] N. Balakrishnan and A. Dalgarno, J. Phys. Chem. A **A105**, 2348 (2001).
[8] J.M. Doyle, B. Friedrich, J. Kim, and D. Patterson, Phys. Rev. A **52**, R2515 (1995).
[9] J.D. Weinstein *et al.*, J. Chem. Phys. **109**, 2656 (1998).
[10] J.D. Weinstein *et al.*, Nature (London) **395**, 148 (1998).
[11] D. Egorov, J.D. Weinstein, D. Patterson, B. Friedrich, and J.M. Doyle, Phys. Rev. A **63**, 030501 (2001).
[12] B. Friedrich *et al.*, J. Chem. Soc., Faraday Trans. **94**, 1783 (1998).
[13] J.L. Bohn, Phys. Rev. A **62**, 032701 (2000).
[14] A.V. Avdeenkov and J.L. Bohn, Phys. Rev. A **64**, 052703 (2001).
[15] S.Y.T. van de Meerakker, R.T. Jongma, H.L. Bethlem, and G. Meijer, Phys. Rev. A **64**, 041401 (2001).
[16] A. Volpi and J. L. Bohn, Phys. Rev. A **65**, 052712 (2002).
[17] G.C. Groenenboom and I.M. Struniewicz, J. Chem. Phys. **113**, 9562 (2000).
[18] S.M. Cybulski *et al.*, J. Chem. Phys. **104**, 7997 (1996).
[19] M. Mizushima, *The Theory of Rotating Diatomic Molecules* (Wiley, New York, 1975), p. 170.
[20] R.S. Freund, T.A. Miller, D. De Santis, and A. Lurio, J. Chem. Phys. **53**, 2290 (1970).
[21] G. Cazzoli and C. Degli Esposti, Chem. Phys. Lett. **113**, 501 (1985).
[22] A.M. Arthurs and A. Dalgarno, Proc. R. Soc. London, Ser. A **256**, 540 (1960).
[23] M. S. Child, *Molecular Collision Theory* (Dover, Mineola, NY, 1996), p. 100.
[24] B.R. Johnson, J. Comput. Phys. **14**, 445 (1973).
[25] E.G.M. van Kempen, S.J.J.M.F Kokkelmans, D.J. Heinzen, and B.J. Verhaar, e-print cond-mat/0110610 (2001).