

Multiquantum vibrational transitions in $O_2(v \geq 25) + O_2(v = 0)$ collisions

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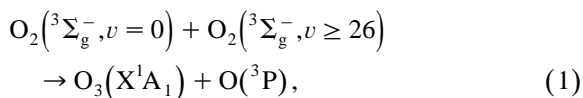
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Abstract

The quenching of highly vibrationally excited O_2 in collision with $O_2(v = 0)$ is investigated using a semiclassical wave packet method. We find that nonreactive collisions dominate the relaxation of $O_2(v)$ and for v in the range 25 to 30 the reactive channel makes little contribution to the quenching process, in agreement with our earlier investigation. We report vibrational transition cross sections and relaxation rate coefficients for $v = 25$ to 30 of the excited $O_2(v)$ molecule. Our study shows that a multiquantum process involving a $2 \rightarrow 1$ vibrational transition which has not been included in previous calculations makes an important contribution to the rate coefficients for the relaxation of O_2 vibrational levels $v \geq 27$. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Vibrationally excited $O_2(^3\Sigma_g^-, v)$, produced in the ultraviolet photolysis of ozone, followed by the reaction



has been proposed as an important source of ozone in the stratosphere [1–5]. The suggestion stemmed from measurements of the quenching of vibrationally excited O_2 that showed a large increase in the destruction rate above $v = 26$ where reaction (1) becomes exothermic.

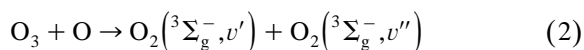
There have been several theoretical investigations. Balakrishnan and Billing [6] used a semiclassical wave packet method with the double many-body expansion (DMBE) potential energy surface (PES)

of Varandas and Pais [7] and found no evidence of chemical reactivity for $27 \leq v \leq 30$. Varandas and Wang [8] used a quasiclassical trajectory method on the same DMBE surface that showed some reactivity for $v = 27$ but only at collision energies much higher than those of the experiments [1,4]. Subsequent reduced dimensional quantum mechanical calculations by Hernández et al. [9] with the DMBE PES and by Lauvergnat and Clary [10] using a newly constructed PES reached the same conclusion as Balakrishnan and Billing [6] that the reactive channel (1) makes a negligible contribution to the destruction of vibrationally excited O_2 at stratospheric temperatures.

Before reaction (1) had been proposed as a source of ozone, the contribution of nonreactive channel to the quenching of vibrationally excited O_2 had been investigated by Billing and Kolesnick [11] for $v \leq 20$ using a semiclassical method with a simple form of

PES that did not allow for reactive collisions. Their results were confirmed by experiments of Price et al. [1] and Park and Slinger [12]. A more sophisticated analysis has been reported by Hernández et al. [13] who used an infinite order sudden approximation method with a more refined PES. Hernández et al. did not find the sharp increase in the relaxation rate coefficient for $v \geq 26$ that was discovered in the experiments [1]. Their study was restricted to single quantum transitions and it employed a PES that did not permit reactive scattering. Multiquantum transitions may occur with high efficiency as indicated in the relaxation of vibrationally excited O_2 in collisions with CO_2 , O_3 and N_2 [14] and in the collisions of CO with CO [15]. Their efficiency may be enhanced as the transitions become more nearly resonant or the energy of the vibrational level approaches the energy at which the reactive channel opens.

We explore here the influence of multiquanta transitions in the presence of reactive channels on the quenching of $O_2(v)$ for vibrational levels lying below and above the reaction threshold. We use DMBE PES because it is six-dimensional and allows for the occurrence of chemical reaction. Calculations with the surface have yielded rate coefficients in agreement with measurements on the reverse reaction [6,7,16–18]



although the theory is less successful in predicting the ro-vibrational distribution of the products [17,18].

2. Methodology

We employ a hybrid quantum-classical approach similar to that used in studies of chemical reactions between diatomic molecules [6]. It has been applied successfully to the benchmark systems OH + H_2 [19,20] and OH + CO [21] and to the relaxation of vibrationally excited CO where the importance of multiquantum transitions was demonstrated [15]. The method involves a quantum mechanical description of the vibrational motions of the two molecules and a classical mechanical treatment of the relative translational and rotational motions. The quantum dynamics is solved by discretizing the vibrational wave-

function on a spatial grid and propagating it in time and space by integrating the time-dependent Schrödinger equation. The quantum and classical dynamics are coupled by an effective Hamiltonian obtained by taking the expectation value of the semiclassical Hamiltonian with the instantaneous wavefunction for the evolution of the quantum degrees of freedom [19,20].

Earlier [6], we used a uniform grid to discretize the vibrational wavefunction. Due to the highly oscillatory nature of the wavefunctions for high-lying vibrationally excited states, a large number of uniform grid points is needed to describe adequately the wavefunctions which severely limited the number of vibrational levels probed and the number of trajectories that could be computed. In this study, we use a discrete variable representation (DVR) based on the Morse oscillator quadrature for the vibrational wavefunctions. The DVR with the associated quadrature scheme provides a more efficient representation of the wavefunction with fewer grid points. The potential energy operator is diagonal in the DVR and its action on the wavefunction is a multiplication by the potential evaluated at the quadrature points. The kinetic energy part of the Hamiltonian is diagonal in the finite basis representation (FBR) which is related to the DVR by a unitary transformation [22].

3. Results and discussion

For the calculations reported here, one of the oxygen molecules was kept in the ground vibrational state and is denoted as O_2 and the other in an excited vibrational state denoted as $O_2(v)$. The vibrational wavefunctions are obtained as an expansion in Morse oscillators using an RKR potential for O_2 with the spectroscopic parameters taken from Ref. [23]. We used Morse oscillator functions instead of Hermite polynomials or other functions that form a complete set because the Morse oscillator more closely resembles the actual wavefunction and only a few extra terms in the basis beyond those needed to include a given vibrational level are necessary for convergence. We have verified that we obtain the same results if an expansion in Hermite polynomials is used with the larger number of basis functions it

requires. We have used an expansion involving five Morse oscillators to represent the wavefunction for O_2 and an expansion with 50 Morse oscillators for $O_2(v)$. The number of DVR points was chosen to be the same as the number of basis functions. Due to the large numerical requirements for the calculations and because we are specifically concerned with the quenching rates of vibrational levels close to the threshold for the bimolecular exchange reaction, we have restricted the vibrational levels probed to the range $v = 25$ to 30.

In the calculations, the initial rotational quantum number of the molecules was taken to be 8, the most probable value at 300 K but the calculated rate coefficients are not sensitive to the initial J value. The impact parameter b was sampled between zero and a maximum value of 5 Å and the initial center of mass separation of the molecules was taken to be 10 Å. The Hamilton equations of motion for the classical variables were solved using a fifth order Runge-Kutta method. The time-dependent Schrödinger equation was solved using the Lanczos method [24]

employing the DVR-FBR scheme to evaluate the operation of the Hamiltonian on the wavefunction. The transition probabilities to distinct final vibrational levels were obtained by projecting the final wavefunction on to the individual O_2 vibrational eigenfunctions. The propagation was terminated and the projection on to the final states was performed when the center of mass separation after the scattering exceeded the initial value. A larger value of 20 Å for the initial and final center of mass separation gave the same results. The cross sections reported here were obtained by averaging the results from 300 trajectories for each energy and have a statistical uncertainty of 20–30% resulting from the Monte-Carlo procedure.

We consider the following energy transfer processes: a single quantum vibration–translation (VT) process, a single quantum vibration–vibration (VV) process and a multi-quantum VV process involving a $2 \rightarrow 1$ vibrational transition. In Figs. 1–3 we show the cross sections for v in the range 25 to 30 as functions of kinetic energy. The multi-quantum transi-

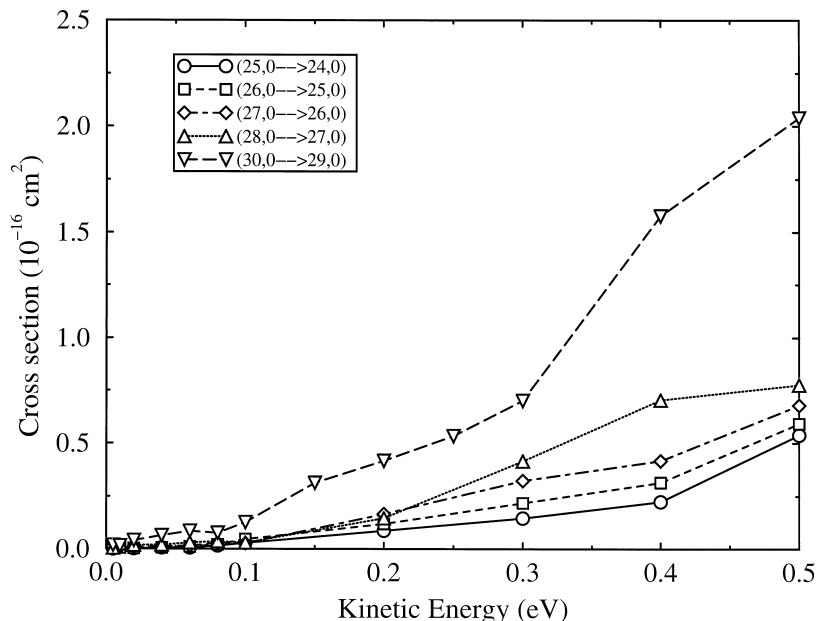


Fig. 1. Cross sections for single quantum VT transitions as a function of kinetic energy for different initial vibrational levels of the excited O_2 molecule. The pairs of numbers within braces in the inset show the initial and final vibrational quantum numbers of the two O_2 molecules.

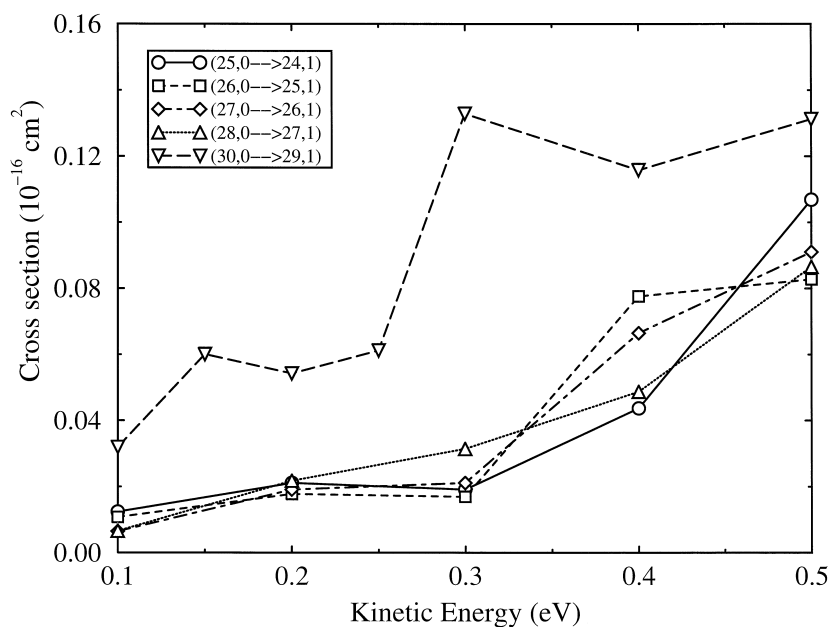


Fig. 2. Cross sections for single quantum VV transitions as a function of kinetic energy for different initial vibrational levels of the excited O_2 molecule. The pairs of numbers within braces in the inset show the initial and final vibrational quantum numbers of the two O_2 molecules.

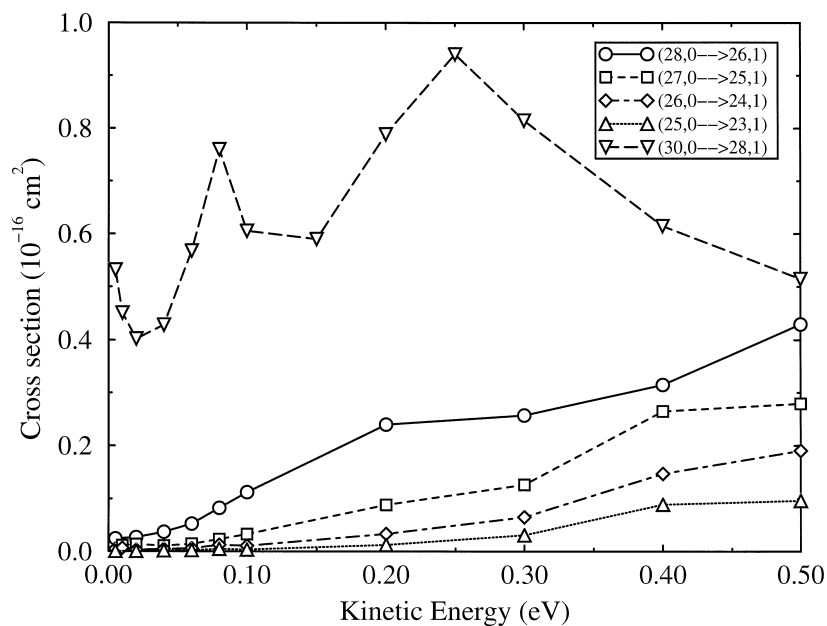


Fig. 3. Cross sections for the $2 \rightarrow 1$ VV transitions as a function of kinetic energy for different initial vibrational levels of the excited O_2 molecule. The pairs of numbers within braces in the inset show the initial and final vibrational quantum numbers of the two O_2 molecules.

tion involves a two quanta loss for the vibrationally excited molecule and a one quantum gain for the vibrationally ground state molecule. For $v = 25$ the VT process is the major quenching mechanism. However, as seen from Fig. 3, the $2 \rightarrow 1$ VV process becomes more efficient as v is raised and for $v = 28$, its cross sections are larger than that of the VT process for energies below 0.2 eV. The enhancement of the $2 \rightarrow 1$ VV process is even more dramatic for $v = 30$ and it dominates the VT process for energies below 0.3 eV, which is the region where the main contribution to the rate coefficients below a temperature of 500 K arises. The single quantum VV transition cross sections are much smaller and they make only a minor contribution to the quenching process though its cross sections for $v = 30$ also show a dramatic increase over the cross sections for lower v . The large enhancements for the $2 \rightarrow 1$ VV transition for $v = 28$ and 30 is due to the smaller energy mismatch compared to other vibrational levels. The energy mismatch for the $2 \rightarrow 1$ VV transition is 435 cm^{-1} for $v = 25$ and 118 cm^{-1} for $v = 30$.

Though our calculation allows for the possibility, we find no evidence of chemical reactivity at the

kinetic energies investigated here, in accordance with our earlier findings [6]. Recently, Varandas and Wang [8] found that the threshold for chemical reaction between $\text{O}_2 + \text{O}_2(v = 27)$ is 1.08 eV, so that the reaction would make little contribution to the rate coefficients below 500 K. Further, Hernández et al. [9] investigated the reaction (1) on the DMBE PES using a reduced dimensional quantum mechanical approach for v in the range 26–34 and obtained rate coefficients several orders of magnitude smaller than the measured values.

In Fig. 4, we compare the computed rate coefficients as a function of v at $T = 460 \text{ K}$ with the experimental results of Price et al. [1]. The ratios between the experimental results and the computed values for v from 25 to 28 are 0.44, 0.41, 1.43, and 11.0 in that order. Thus calculated and experimental rate coefficients for v from 25 to 27 are within a factor of 2 but for $v = 28$ the predicted result is an order of magnitude smaller than the measured value. For $v = 30$, the computed result is about half the experimental value for $v = 28$. The $2 \rightarrow 1$ VV transition is an important contributor to the quenching process, accounting for half the rate coefficient for

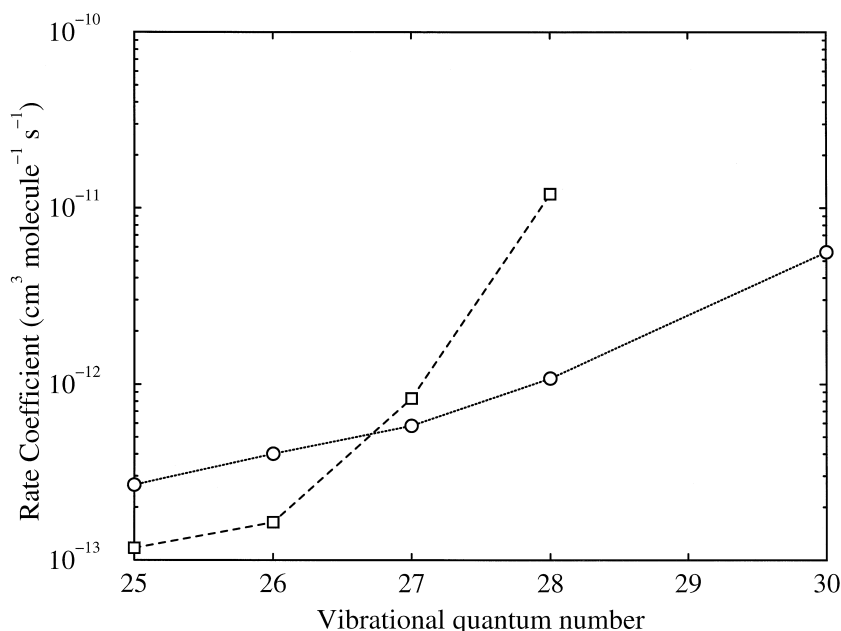


Fig. 4. Rate coefficients for the quenching of $\text{O}_2(v)$ by $\text{O}_2(v = 0)$ as a function of vibrational quantum number v at $T = 460 \text{ K}$. Computed values are shown by open circles and measured values [1] by open squares. The dotted and dashed lines connecting the symbols are only to guide the eye.

$v = 27$ and a factor of 0.7 of it for $v = 28$. For $v = 30$ it is the dominant quenching mechanism.

Previous theoretical studies [6,8,9] on different PESs and dynamics treatments have shown that the reactive channel makes little contribution to the quenching of $O_2(26 \leq v \leq 30)$. The present study has focused on nonreactive collisions. Though our study does not reproduce the measured sharp increase in the relaxation rate coefficient for $O_2(v = 28)$, it does point out that the near resonant $2 \rightarrow 1$ vibrational transitions make significant contributions to the rate coefficients for $v \geq 27$. The change in the slope of the computed rate coefficients for $v > 27$ is due to this process. As theoretical studies of both the reactive and nonreactive channels are unable to explain the sharp increase in the rate coefficient for the quenching of $v = 28$, there remains the interesting question as to the cause of the measured rapid quenching of the $v = 28$ level and the identification of the end-product.

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