O+OH→O₂+H: A key reaction for interstellar chemistry. New theoretical results and comparison with experiment

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(Received 17 November 2009; accepted 24 November 2009; published online 10 December 2009)

We report extensive, fully quantum, time-independent (TID) calculations of cross sections at low collision energies and rate constants at low temperatures for the O+OH reaction, of key importance in the production of molecular oxygen in cold, dark, interstellar clouds and in the chemistry of the Earth’s atmosphere. Our calculations are compared with TID calculations within the J-shifting approximation, with wave-packet calculations, and with quasiclassical trajectory calculations. The fully quantum TID calculations yield rate constants higher than those from the more approximate methods and are qualitatively consistent with a low-temperature extrapolation of earlier experimental values but not with the most recent experiments at the lowest temperatures. © 2009 American Institute of Physics. [doi:10.1063/1.3274226]

The exothermic reaction between the O(3P) atom and the OH(7II) radical (Fig. 1) is a major contributor to the production of O₂ in interstellar environments.1,2 This reaction is prototypical of many barrierless neutral-neutral reactions which are thought to play an important role in the cores of cold, dark interstellar clouds.3 The accurate determination of the rate constant for the title reaction at low temperature (10–50 K) is an essential step in the resolution of the so-called interstellar O₂ problem: Measurements4 from the satellite ODIN mission suggest that the abundance of O₂ in the cores of these interstellar clouds is ~1000 times lower than predicted by the latest astrochemical models.5 In addition, the O+OH reaction plays a key role in both the removal of “odd oxygen” in the upper stratosphere and in the formation of highly vibrationally excited OH in the mesosphere, the so-called HO₃ dilemma.6

Above ~200 K there have been many experimental measurements of the rate constant for the O+OH reaction.5,7–9 Notwithstanding the technical difficulty of the low-temperature study of reactions between neutral radicals, recently Carty et al.5 were able to apply the CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) flow technique to the O+OH reaction at T=39–142 K, finding little variation in the rate constant over this range. However, as seen in Fig. 2, the values obtained were significantly lower than would be predicted by extrapolation of measurements at higher temperature.

There is a long history of theoretical studies of the O+OH reaction, to investigate both the fundamental reaction dynamics and to determine accurate rate constants for subsequent kinetic modeling.10–14 Most of these studies have been based on quasiclassical trajectory (QCT) or statistical treatments of the dynamics. Unfortunately, the inability of QCT treatments to conserve the vibrational zero-point energy can render this method unreliable near reaction thresholds,13 as discussed for the O+OH reaction elsewhere.15

The O+OH reaction, which proceeds through the deep HO₂ well, should be amenable to a statistical treatment, based on adiabatic capture considerations.16 However, recent...
The O2 product and because many partial waves contribute.\footnote{\textsuperscript{22} TID+J-shifting} Scattering calculations on accurate \textit{ab initio} \textsuperscript{50} accessible vibration-rotation states of the HO2 complex and of actions of the O+OH reaction are far more computationally demanding because of the large number of energetically accessible vibration-rotation states of the HO2 complex and of the O\textsubscript{2} product.\footnote{\textsuperscript{50}}\footnote{\textsuperscript{22}}\footnote{\textsuperscript{19}}

Correctly, as an open-shell diatomic in the rotational averaging.\footnote{\textsuperscript{22}}

Work has revealed that reaction is inhibited by the presence of a strong dynamical bottleneck.\footnote{\textsuperscript{13}15,17} This is ignored in statistical treatments, leading to an overestimation of the reaction probability.\footnote{\textsuperscript{14}}\footnote{\textsuperscript{15}}\footnote{\textsuperscript{17}}

In principle, high-accuracy predictions could be achieved by fully quantum, time-independent (TID) reactive scattering calculations on accurate \textit{ab initio} potential energy surfaces (PESs), such as have been successfully applied to the paradigm F+H\textsubscript{2} reaction.\footnote{\textsuperscript{18}}\footnote{\textsuperscript{21}}\footnote{\textsuperscript{22}} Regrettably, TID investigations of the O+OH reaction are far more computationally demanding because of the large number of energetically accessible vibration-rotation states of the HO\textsubscript{2} complex and of the O\textsubscript{2} product and because many partial waves contribute.

To circumvent the difficulty of full TID calculations, several groups have applied\footnote{\textsuperscript{19,20}} the “J-shifting” approximation\footnote{\textsuperscript{21,22}} in which TID calculations are carried out for only a single, minimal value of the total angular momentum and then repeatedly shifted up in energy to simulate the full dependence of the reaction cross sections on the total angular momentum. Unfortunately, as will be shown here, there is considerable inaccuracy in the use of the J-shifting approximation at low energies.

Lin and Guo used a computationally more efficient wavepacket (WP) technique to the O+OH reaction\footnote{\textsuperscript{14}} and to its reverse.\footnote{\textsuperscript{25}}\footnote{\textsuperscript{22}}\footnote{\textsuperscript{21}}\footnote{\textsuperscript{22}}\footnote{\textsuperscript{25}} At low temperature the rate constants calculated by this method are smaller than those measured by Carty \textit{et al.}\footnote{\textsuperscript{5}} and thus in further disagreement with the low-temperature extrapolation of the measurements at room temperature and above. However, it is well known that the WP method may not be accurate at low collision energies because of difficulties in damping outgoing waves with long de Broglie wavelengths.

Because of the importance of the O+OH reaction, full quantum TID calculations, free of approximations, must be done to resolve the discrepancy between the results of the various, approximate theoretical methods, between these and experiment, and between the low-temperature experiments and the extrapolation of those at higher temperatures. Theory could then partner with laboratory based experiments to provide unambiguous input into models, aimed at resolving the interstellar O\textsubscript{2} problem. To this end, we describe here new, extensive, converged TID calculations of low-energy cross sections and low-temperature rate constants for the O+OH reaction.

In our investigation of the scattering dynamics we use the latest version of the XXZLG PES of Xu \textit{et al.}, which is a three-dimensional, cubic-spline interpolant of \textgreater{}18 000 \textit{ab initio} points on the PES of the lowest (\textit{X} \textsuperscript{2}A\textsubscript{u}\textsuperscript{+}) state of the HO\textsubscript{2} system.\footnote{\textsuperscript{20}}\footnote{\textsuperscript{24}} Also, as in all recent investigations of the OH+O reaction, in the scattering calculations we ignored the electronic orbital and spin angular momenta, assuming that the rotational level structure of the reactant (OH) and product (O\textsubscript{2}) diatomics was that of a closed-shell molecule.

The first set of calculations used the J-shifting approximation discussed earlier.\footnote{\textsuperscript{22}} The OH(v=0,j)+O reaction probability for all values of the total angular momentum J\textgtr j is approximated by

\begin{equation}
\mathcal{P}_j^{(E)}(E_c) = \mathcal{P}_j^{(E)}[E_c - E_j^{(j)}].
\end{equation}

Here, E\textsubscript{c} is the collision energy and E\textsubscript{j}^{(j)} is the energy shift, defined as the height of the long-range centrifugal barrier at large OH–O distances, which increases with increasing J. Equation (1) allows the reaction cross section, which is the weighted sum of the J-dependent reaction probabilities, to be determined by just those for J\textgtr j. In our application of the J-shifting approximation, we used the ABC code of Manolopoulos and co-workers\footnote{\textsuperscript{26}} to determine exact probabilities for the O+OH reaction for values of the total angular momentum J=0–5. In these calculations we retained all allowed values of the rotational projection quantum number K. Reaction probabilities were determined on a 500-point grid in collision energy ranging from 5 \times 10\textsuperscript{-4} to 0.25 eV for values of the initial OH rotational quantum number j ranging from j=0 to j=5. In the J-shifting results reported here we corrected several small errors in the earlier use of this approximation by Xu \textit{et al.}\footnote{\textsuperscript{20}}

Finally, we used the ABC code\footnote{\textsuperscript{25}} to carry out TID quantum reactive scattering calculations for all values of J that made a nonzero contribution to reaction on a finer grid of energies (N=40), ranging from 2.4 \times 10\textsuperscript{-4} to 0.038 eV. An exhaustive number of convergence studies preceded the production calculations. Converged integral reactive cross sections could be obtained by including K\leq 12 for J\geq 30 and K\leq 16 for J>30. Even with this restriction on K, the TID calculations were extremely computationally intensive. The largest calculations involved more than 9000 channels. In addition, we carried out standard QCT calculations.\footnote{\textsuperscript{26}}

From the cross sections we determined thermal rate constants, by integrating over a Maxwellian distribution of collision energies. Since only two of the 36 O+OH states will react over the attractive \textit{X} \textsuperscript{2}A\textsubscript{u}\textsuperscript{+} PES, the calculated reaction cross sections and rate constants are reduced by multiplica-
actions predicts an increase in the cross section with decreasing collision energy,\textsuperscript{16,19} here the rate constant decreases at temperatures below $\sim 50$ K. The explanation is quite simple: The rate constant is the Maxwellian average of the reactive flux—the product of the cross section times the collision velocity. The increase in the OH+O cross section at low velocity is not rapid enough to compensate the decrease in the velocity.

Our benchmark TID calculations, which provide the most accurate description of the reaction dynamics, predict rate constants at low temperature which are 20%–30% larger than those predicted by calculations within the J-shifting approximation and nearly a factor of 2 larger than those predicted by the QCT method. Figure 3 shows that, at least for reaction of OH($j=0$), the WP method is even less accurate at these low energies.

Our results here demonstrate that only full TID calculations can accurately characterize chemical reactions at cold and ultracold temperatures, an area of considerable current research interest.\textsuperscript{19} Unfortunately, such calculations are the most computationally intensive. We also note that J-shifting\textsuperscript{19} will be inaccurate at all but the lowest energies, where only the $J=0$ partial wave will contribute. Figure 2 also casts further confusion on the interpretation of the several experimental investigations of the rate constant for the O+OH reaction at room temperature and below.\textsuperscript{5,7,8} In particular, the temperature dependence predicted by our TID calculations are qualitatively consistent with a low-temperature extrapolation of the earlier experimental values over the range 150–300 K, but not with the most recent experiments at the lowest temperatures.\textsuperscript{5}

However, independently of the way in which the reaction dynamics is treated, the present calculations show that compared with experiment at temperatures above $\sim 150$ K, theory underpredicts the rate constant for the O+OH reaction. This may be a consequence of deficiencies in the \textit{ab initio} PES used, although the underlying calculations were of sophistication comparable to the methods used in the determination of the PES for the F+H$_2$ reaction, where excellent agreement with experiment was seen, even at the state-to-state level.\textsuperscript{18}

Another source of error is the neglect of the spin and electronic fine structure of the OH and O reactants. The size of this error is likely illustrated by the two sets of composite TID+J-shifting curves in Fig. 2, in which we use both the closed-shell and the correct open-shell expressions for the energies and degeneracies of the lowest rotational levels of OH. In the latter case a larger weight is assigned to the reaction cross section out of the lowest rotational level of OH.

Finally, there is the possibility of nonadiabatic transitions. Although the PES corresponding to the lowest $^2$A$'$ state correlates only with the energetically inaccessible H + O$_2$(a $^1\Delta_g$) product channel (Fig. 1), it is possible for reactants to enter without a barrier into the well associated with the electronically excited state of the HO$_2$ complex. Nonadiabatic electronic relaxation of this complex—internal conversion—can provide an additional pathway for production of O$_2(X^3\Sigma_g^{-})$+H($^3S$) products, as illustrated schemati-
cally by the curved arrow in Fig. 1. The $\tilde{X}^{2}A''$ and $\tilde{A}^{2}A'$ states become a degenerate $^{2}II$ state in linear geometry—a Renner–Teller pair. The coupling between them has been studied in the region of the triatomic minimum,28 but not as yet in the region(s) of the PESs which may make the largest contribution to the O+OH reaction. Although TID investigations of the OH+O reaction on multiple, coupled PESs is not yet computationally feasible, preliminary study suggests that this nonadiabatic coupling will be small, although spin-orbit coupling between the two states may contribute.29

The present calculations demonstrate our ability to carry out fully quantum reactive scattering calculations for reactions involving two heavy (nonhydrogen) atoms, of accuracy and precision comparable to those for reactions involving one heavy atom.18 Despite this achievement, below room temperature there remains considerable disagreement between theory and experiment, and, also, between the results of different experimental techniques. In view of the difficulty of the experimental study of radical-radical reactions at low temperature, theoretical calculations may provide the most accurate means to predict the low-temperature dependence of rate constants for the OH+O, and other astrophysically important, few-atom, reactions. We would urge the use of our theoretical rate constants in future modeling studies.

Because the O+OH reaction plays a key role in the production of the chemically important oxygen molecule in astrochemical environments, and because the observed abundance of O$_2$ is so much smaller than predicted by astrochemical modeling, theory and experiment must work toward greater consistency and accuracy in understanding the low-temperature rate for this reaction.

For computational support, we thank the College of Chemical and Life Sciences, University of Maryland and the Pôle de Sciences Planétaires Bourgogne Franche-Comté, M.H.A. and H.G. are supported by the Department of Energy (Grant Nos. DE-SC0002323 and DE-FG02–05ER15694), and D.X. by the National Natural Science Foundation of China (Grant No. 20725312) and the Ministry of Science and Technology of China (Grant No. 2007CB815201).

29W. Eisfeld (private communication).