Semiclassical wave packet study of ozone forming reaction

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We have applied the semiclassical wave packet method (SWP) to calculate energies and lifetimes of the metastable states (scattering resonances) in a simplified model of the ozone forming reaction. All values of the total angular momentum up to =50 were analyzed. The results are compared with numerically exact quantum mechanical wave packet propagation and with results of the time-independent WKB method. The wave functions for the metastable states in the region over the well are reproduced very accurately by the SWP; in the classically forbidden region and outside of the centrifugal barrier, the SWP wave functions are qualitatively correct. Prony's method was used to extract energies and lifetimes from the autocorrelation functions. Energies of the metastable states obtained using the SWP method are accurate to within 0.1 and 2 cm^{-1} for under-the-barrier and over-the-barrier states, respectively. The SWP lifetimes in the range of 0.5 □ / □ 100 ps are accurate to within 10%. A three-level model was used to investigate accuracies of different approximations for the reaction rate constant. It was shown that the majority of the metastable states in this system are either long lived (narrow resonances)

produce an important isotope effect. It has also been shown that one can account for this effect by introducing (based on qualitative arguments related to difference in statistical density of states in symmetric and asymmetric O_3 isotopomers) a simple correction factor into statistical[15] or classical trajectory[26] treatments and tuning this factor to fit the experimental results. Note that the metastable ozone states O_3^* play the central role in the isotope effects in both processes (2) and (3).

Although the progress in understanding the basic mechanisms of the isotope effect at a qualitative level has been impressive and we, perhaps, can say that the molecular origin of anomalous isotope effects has finally been identified, a quantitative theoretical treatment of the processes (2) and (3) is still lacking. It is fair to say that none of the existing theories of ozone formation reaction are both rigorous and complete: The RRKM-based theory,[15] apart from its statistical assumptions, lacks information about the ozone PES and involves an empirical treatment of symmetry. The classical trajectory method[26] is able to show the isotope effects only when these effects are expected and the desired quantum properties have been built into the classical formalism

. Such an approach cannot be regarded as based on the first principles. The quantum mechanical theories proposed so far are prohibitively expensive computationally and therefore either focused only on the first step (2) and thereby restricted to nonrotating (total angular momentum quantum number $=0$) ozone molecules,[20,21] or limited by reduced dimensionality and sudden approximation assumptions for collision and vibration-rotation,[17] which are not valid for slow processes (2) and (3) where the relative motion of nuclei is rather adiabatic than sudden.

A theoretical method suitable for description of the isotope effects in (2) and (3) should account for all features of the complicated ozone PES,[19] incorporate full dimensionality of the problem, avoid using sudden approximations, be able to treat scattering resonances, and also include the quantum ZPE and quantum symmetry in a rigorous way. We think that the semiclassical wave packet (SWP) method, also known as the Herman-Kluk propagator[31–34] or as the initial value representation method,[35–37] might be a good approach for this problem. It takes into account all features of the PES in a natural, dynamic way; dimensionality of reactions (2) and (3) is not a problem for this trajectory-based method, and no sudden-type approximations are necessary. It is also well established that the SWP approach describes the quantum zero-point energy[37,38] and is able to reproduce quantum symmetry,[39] particularly the symmetry effects in state-to-state transitions in processes similar to the ozone forming reaction.[29]

Much less is known about the ability of the SWP approach to deal with quantum scattering resonances such as those in O_3^*. In the SWP study of collinear $H+H_2$ reactive scattering, significant oscillations in the state-to-state transition probabilities have been observed[40–42] and attributed to wide overlapping scattering resonances, but the resonances themselves were not characterized. In another study of col-

III. SWP CHARACTERIZATION OF SCATTERING RESONANCES

The semiclassical wave function in Eq. (11) can be used to calculate the autocorrelation function

$$( ) = \langle \square(,0) | \square(,) \rangle \tag{13}$$

and the half spectrum

$$( ) = \left| \int_0^{\square} ( ) \exp\{ \quad \} \right|^2 . \tag{14}$$

The energy spectrum of potential (4) contains both bound and metastable states. The bound states are characterized by real negative energies $\square 0$ and real wave functions $\square$

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determined exclusively by the excitation energy of the metastable O_3^*. Only in the intermediate regime, when

again, the results of SWP and WKB methods agree very well. At some values of the SWP result slightly exceeds the result of WKB, while at other values of the result of WKB is somewhat larger. But these differences compensate each other almost entirely when the sum (44) over all values of is calculated.

V. CONCLUSIONS

In this work we demonstrated that the SWP method can be successfully applied to calculate energies and lifetimes of the metastable states trapped behind the centrifugal barrier. Such metastable states play a central role in many recombination reactions, including the ozone forming