

Does the “Reef Structure” at the Ozone Transition State towards the Dissociation Exist? New Insight from Calculations and Ultrasensitive Spectroscopy Experiments

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Since the discovery of anomalies in ozone isotope enrichment, several fundamental issues in the dynamics linked to the shape of the potential energy surface in the transition state region have been raised. The role of the reeflike structure on the minimum energy path is an intricate question previously discussed in the context of chemical experiments. In this Letter, we bring strong arguments in favor of the absence of a submerged barrier from ultrasensitive laser spectroscopy experiments combined with accurate predictions of highly excited vibrations up to nearly 95% of the dissociation threshold.

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Dissociation and recombination properties related to stratospheric ozone depletion are attracting increasing interest to high-energy states of this molecule shielding Earth from harmful UV radiation [1–3]. Because of the quite complicated electronic structure of this seemingly simple triatomic [1,4–7], many features of the dynamics of ozone formation are far from being understood. One is the discovery of the mass-independent fractionation [8–10] which is “a well-recognized milestone in the study of isotope effect” [11] and a “fascinating and surprising aspect . . . of selective enrichment of heavy ozone isotopomers in the atmosphere and in laboratory settings” [6]. This is linked to intricate questions of isotope dependence of ozone formation rates for which the interpretation is not yet fully satisfactory. Several fundamental issues raised by ozone studies could have an impact on the understanding of important phenomena in quantum molecular physics and of the complex energy transfer dynamics near the dissociation threshold. Troe *et al.* [12] introduced a “chaperon mechanism” for the recombination processes, and Marcus [11] explored ideas of energy sharing through accidental vibration-rotation resonances being counterparts of classical bifurcations and a possible role of symmetry breaking. van der Waals states [13], metastable states [14], and Feshbach-type resonances [15,16] have been considered in this context.

The minimum energy path (MEP) towards the dissociation goes through a bottleneck of the potential energy surface (PES). The corresponding transition state (TS) region [1,4–6,17,18] plays a key role in the modeling related process. A bird’s-eye view on the stretching-bending cut of the ozone ground electronic state PES is shown in Fig. 1(b). The dissociation PES limit is $D_e = 9220 \text{ cm}^{-1}$

and $D_0 = 8564 \text{ cm}^{-1}$. The TS range extends from ~ 3 to 6 a.u. for the longer O-O distance: in this range, the electronic structure changes significantly, causing the other O-O bond to shrink from $R_e(\text{O}_3) = 2.4 \text{ a.u.}$ to $R_e(\text{O}_2) = 2.28 \text{ a.u.}$

Most high-level *ab initio* studies on the electronic structure carried out during many years have predicted that the MEP shape should exhibit a “reeflike” structure [1,4,5,13,14] with a submerged barrier below the dissociation limit. Since then, that reef feature has been taken as a true signature of the ozone PES. The important impact of the barrier on the formation and fragmentation dynamics has been discussed in several investigations (Schinke *et al.* [1], Dawes *et al.* [6], and references therein). These studies suggested that the rate coefficient of isotope exchange reactions should be very sensitive to the PES shape in the TS region. As a consequence of the reef feature, the calculated rate constants were 3–5 times smaller than measured ones and had the wrong temperature dependence [1].

The question was asked whether this barrier could be an artifact of available *ab initio* calculations. Schinke *et al.* [1] found that an artificial removal of the reef structure from the PES substantially increased the reaction cross section and brought the calculated rate constants to much better agreement with the experiment. However, it was believed for the past decades that there was no evidence for the absence of this feature from the quantum molecular theory. An important finding concerning this puzzle has been recently reported by Dawes *et al.* [6], who noted that “an avoided crossing with an excited (electronic) state can result in disruptions in the ground state surface seen as a submerged reef.” They claimed that an account for several interacting electronic states in the wave function results in a better

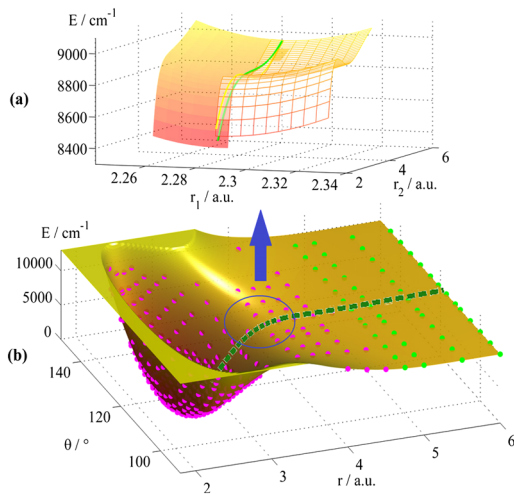


FIG. 1 (color online). The shape of the ozone PESs obtained from *ab initio* calculations. Panel (b) shows a bird's-eye view on the valence-angle section from the equilibrium to the dissociation along the MEP (dashed green line). The TS range (encircled) is blown up at panel (a) where two PES versions are compared: one with the reef barrier at the right-hand side (R_PES) and another one without reef structure (NR_PES) at the left-hand side. Here r_1 , r_2 , and θ are bond length and bond angle internal coordinates: $\theta = 117^\circ$ at (a); $r = r_1$ and $r_2 = 2.4$ a.u. at (b).

description of this region and consequently the reef should disappear [6]. Even if the excited states are not at all close, their inclusion in the optimization of the orbitals and reference space tends to “smooth” the barrier top, producing the “no-reef” effect. Dawes *et al.* were able to derive the thermal rate constant for the exchange reaction by using a quantum statistical model which agrees much better with kinetic experimental data in the absence of this submerged barrier. The role of the narrow incoming TS channel for the kinetics is an important issue to be investigated.

It has been argued [1] that chemical-type experimental data (thermal rate coefficients) are highly averaged quantities and detailed experimental “spectroscopic data slightly below and above the threshold would be instrumental in checking the shape of the PES in the TS region and verifying quantum-mechanical resonance calculations” [1].

Along this line, we provide new insight, bringing strong arguments on the shape of the ozone TS. The aim of this work was validating existing theoretical hypotheses by an extensive set of accurate spectra measurements and analyses compared with theoretical predictions. This is based on a large set of relevant data originating from “physical” experiments: highly excited vibration-rotation energies approaching 95% of the dissociation threshold derived by ultrasensitive cavity-ringdown spectroscopy (CRDS) [19–21]. The motivation was to augment the knowledge of the properties of excited ozone: it is well known that even tiny stationary points on the PES could have significant consequences on the dynamics. The reef behavior has been associated with a bottleneck and the formation of short-lived metastable states which determine the reactivity

and kinetics. A strong link between PES properties and dissociation or association dynamics has been recently highlighted in Refs. [6,22]. Other than that, the analyses of resonance couplings in the observed spectra are expected to bring important information concerning statistical or non-statistical ozone behavior [10,11,23,24] at high energy.

The CRDS spectrometers developed for this project present unique performances in terms of sensitivity, spectral coverage, and linear dynamic range on the intensity scale. By averaging spectra over a small spectral interval, they allowed achieving a record sensitivity for CRDS of $5 \times 10^{-13} \text{ cm}^{-1}$ corresponding to 1% attenuation of the incident light after a 200 000 km path length [21]. A set of 80 distributed feedback laser diodes was used to cover continuously the 5850–7920 cm^{-1} range. The ozone spectra were recorded with a routine noise equivalent absorption $\alpha_{\text{min}} \sim 2 \times 10^{-10} - 5 \times 10^{-11} \text{ cm}^{-1}$, typically 3 orders of magnitude better than for the best Fourier transform spectrometers coupled to multipass cells [25,26]. Figure 2 gives an idea of these experimental achievements: as the intensities of the detected bands decrease very sharply with increasing upper state energies, at the highest edge of our recordings the line strengths are by 8 or 9 orders of magnitude smaller than for the strongest fundamental v_3 band. Experiments were carried out with $^{16}\text{O}_3$ and $^{18}\text{O}_3$ obtained from the quasicomplete conversion of $^{16}\text{O}_2$ and $^{18}\text{O}_2$ at a typical pressure of $P = 20$ Torr, with a silent electric discharge (12 kV, 400 Hz).

Accurate theoretical predictions for band centers and for the vibrational dependence of rotational constants were mandatory for interpreting these very complicated CRDS spectra. At the highest range of observations, we used variational calculations from two versions of our recent *ab initio* PES [17], both computed at a high level of

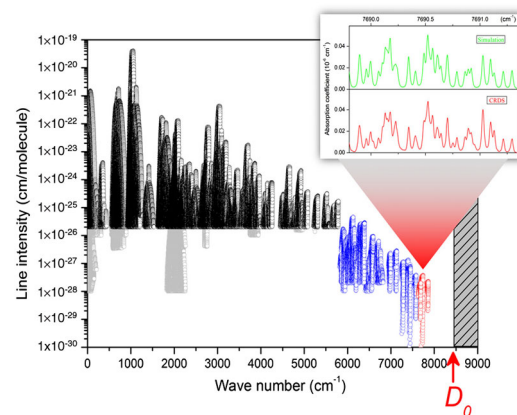


FIG. 2 (color online). Log scale summary for experimental intensities of ozone vibration-rotation transitions showing a necessity of extremely sensitive methods to access the dissociation threshold D_0 . Previously observed data are shown in black with extrapolations in gray [26]. Our CRDS measurements are shown in blue including yet unpublished bands in red. The upper panel gives an example of an agreement of experimental spectra and theoretical simulation resulting from the analyses.

electronic structure theory with the largest basis sets ever used for ozone. The first PES, referred to as R_PES (“reef_PES”), has been obtained by including single electronic state in the orbital optimization and possesses the reef TS feature as most published potentials do.

The second one accounts for Dawes’ finding [6,18] mentioned above via a correction which considers interaction with the excited states. This changed the shape of the bottleneck range along the MEP and transformed the reef to a kind of smooth shoulder [6,17]. This latter potential is referred to as NR_PES (“no_reef_PES”). The major difference between these two PESs appears in the TS range [Fig. 1(a)]: right-hand side for the R_PES and left-hand side for the NR_PES. The height of the reef barrier (at $r_{OO} = 3.96$ a.u.) with respect to the van der Waals well (at $r_{OO} = 4.4$ a.u.) in the R_PES is 35 cm^{-1} . Both PESs have very similar equilibrium configurations and give the same dissociation threshold: the theoretical value for both of them— $D_0 = 1.0548 \text{ eV} \Leftrightarrow 8508 \text{ cm}^{-1}$ —lies between two experimental dissociation energies with a deviation of only 0.6% from the most recent experimental value of Ruscic [27] as quoted in [5]. Figure 1 shows the PES in one of the nuclear configuration sectors with $r_1 < r_3$; $r_2 < r_3$, the two others being obtained by symmetry permutations. A detailed discussion of *ab initio* PES calculations can be found in Ref. [17]. On the bird’s-eye view of the potential on the scale 0–10 000 cm^{-1} [Fig. 1(b)], the difference between R_PES and NR_PES is hardly visible but results in very significant changes for the spectroscopy in the range of highly excited vibrations. New experimental data allow clearly distinguishing between the two shapes of the PES.

Apart from the experimental breakthrough, a considerable challenge was the analyses of complicated experimental spectra. The centers of a rovibrational bands defined as the $J \rightarrow 0$ limit of the upper state energies were accurately determined by following line series in *P*, *Q*, or *R* branches [26] in a large range of *J*, *K_a* values. This implied the full rovibrational assignment of the recorded spectrum. Finally,

in the full CRDS range, 5850–7920 cm^{-1} , a total of 15 489 transitions of 53 bands of $^{16}\text{O}_3$ and $^{18}\text{O}_3$ were assigned, resulting in 8999 upper state experimental vibration-rotation levels [Table I]. The diagram of band centers (vibration levels) deduced from the CRDS spectra is given in Fig. 3. The centers of the seven highest, yet unpublished bands are given in Table I(b). This large sample of states up to $\sim 95\%$ of the dissociation energy represents valuable experimental data for crucial tests of various hypotheses for the shape of the ozone PES in the TS range.

In this work, we have explored the impact of the reef barrier on bound quantum states in this energy range. For spectra interpretation, other than band centers, quite accurate predictions for vibrational dependence of rotational constants and of “dark” perturbing states involved in accidental vibration-rotation resonances were necessary. In this context, we found that it was not possible to make a physically meaningful assignment of the CRDS spectra of ozone above 7500 cm^{-1} by using existing PES possessing a reef feature nor with the latest R_PES version [17] nor with any reef PES available in the literature. Calculated errors were too large for unambiguous band identification.

On the contrary, the predictions from *ab initio* NR_PES (without a reef barrier) are in excellent agreement with experimental data: the *rms* deviation for all band centers is below 1.5 cm^{-1} that is an unprecedented accuracy for multielectron molecules in the range near the dissociation threshold. For comparison the *rms* deviation in band centers computed from the most accurate available reef PES for the same range is 16 cm^{-1} for $^{16}\text{O}_3$ and 17 cm^{-1} for $^{18}\text{O}_3$. Figure 4 shows a clear trend to an overestimation of vibrational energies pushed up by the reef barrier. Although there is still about 650 cm^{-1} until the dissociation, it is clearly seen that the effect of the reef is already pronounced at about 2000 cm^{-1} beneath D_e , the error gradually increasing with energy.

The intermode energy transfer should critically depend on *accidental resonances*, for which no information in the

TABLE I. CRDS measurements of ozone bands in the energy range of TS and comparison with predictions from NR_PES.

(a) Summary for the analyzed transitions in observed spectra							
Iso	Range/ cm^{-1}	<i>Nb</i> bands	<i>Nb</i> lines	<i>Nb</i> levels	J_{\max}	Mean err ν_0/cm^{-1}	<i>rms</i> ν_0/cm^{-1}
$^{16}\text{O}_3$	5850–7880	31	9203	5147	49	0.25	1.21
$^{18}\text{O}_3$	5850–7920	22	6286	3852	48	0.69	1.50
(b) New bands in highest wave number range							
Center: ν_0/cm^{-1}							
Iso	<i>NT</i>	Predicted	Observed	<i>Nb</i> lines	<i>Nb</i> levels	J_{\max}	(Obs – Pred)/ cm^{-1}
$^{16}\text{O}_3$	80 B	7687.22	7686.08	198	92	30	–1.14
$^{16}\text{O}_3$	82 B	7741.15	7739.62	135	83	26	–1.52
$^{16}\text{O}_3$	86 B	7863.32	7860.08	210	121	26	–3.24
$^{18}\text{O}_3$	86 B	7505.89	7503.40	75	48	23	–2.49
$^{18}\text{O}_3$	90 B	7632.18	7629.53	176	131	30	–2.65
$^{18}\text{O}_3$	96 B	7752.03	7752.70	136	79	26	0.67
$^{18}\text{O}_3$	101 B	7910.41	7908.84	80	58	21	–1.57

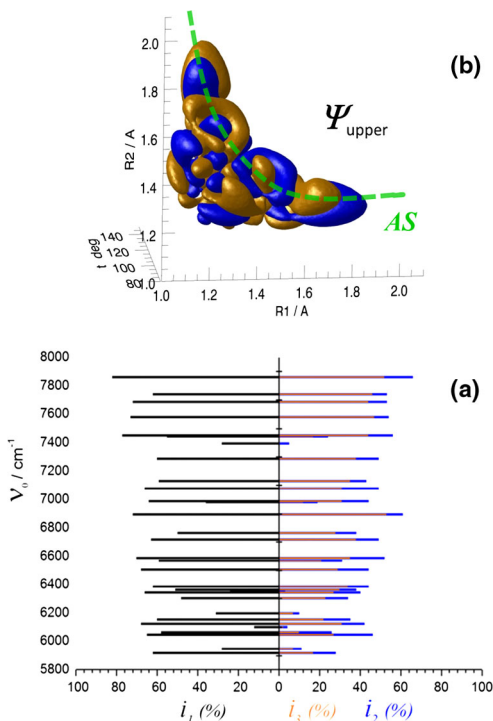


FIG. 3 (color online). (a) $^{16}\text{O}_3$ band centers (ν_0) deduced from CRDS spectra and their rectilinear normal mode inflation coefficients: contributions beyond the first major term (left panel) and those beyond two and three major terms (right panel). (b) The shape of 3D vibrational wave function Ψ corresponding to our highest observed $^{16}\text{O}_3$ band at $\nu_0 = 7860 \text{ cm}^{-1}$. Though high states do not have pure normal mode character, it is clearly seen that Ψ probes nonlinear MEP [17] corresponding to asymmetric stretch (AS) orbit in the TS range: dashed green curve.

high-energy range was available prior our study. The important point is that inflation of normal modes dramatically increases with energy when approaching the TS range (Fig. 3) due to accidental anharmonic coupling making vibrational motion more “stochastic” in classical terms [28]. For each vibrational state, the normal mode inflation coefficients $i_m(\%) \equiv 100 \times i_m$ indicate the contributions that remain beyond m leading normal mode terms: $i_1 = 1 - C_1^2$, $i_2 = 1 - (C_1^2 + C_2^2)$, Here C_1 is the major coefficient of the vibrational wave function expansion in the normal mode basis, C_2 is the second one and so on, these coefficients being calculated by the method described in Ref. [29]. If all i_m are small, this means that the state has a pure normal mode character. If only i_1 is large ($\sim 50\%$), this could correspond to one localized resonance of two coupled states, but if i_1, i_2, i_3, \dots are large, this means that no dominant normal mode contributions occur. Figure 3 shows that this is clearly the case of many highly excited states. However, there exist few “stability islands” of a regular vibrational motion (small values of i_m in Fig. 3). Previously available high-energy experiments of Chang *et al.* [30] mostly sampled excited symmetric stretch states nv_1 (having almost vanishing normal mode inflation $i_m \sim 0$) that did not bring information on the dissociation

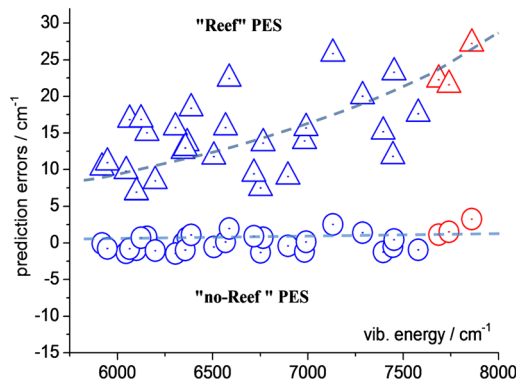


FIG. 4 (color online). Discrepancies (Calc. - Obs.) between $^{16}\text{O}_3$ band centers observed in our CRDS spectra and theoretical predictions from two *ab initio* PESs [17] in the range approaching the dissociation threshold for the same energy ranking numbers. Circles correspond to NR_PES and triangles to R_PES. Centers of three newly observed bands at the highest interval are given in Table I.

channel. On the contrary, the wave function corresponding to our highest observed vibrational state of $^{16}\text{O}_3$ (Fig. 3) clearly samples excited asymmetric stretch vibrations with multiple nodes along the reaction coordinate towards the TS range. An ongoing prospective is to study the impact of symmetry-breaking isotopic substitutions on wave functions that could be a factor of the η -effect in the mass-independent isotope fractionation [10,11,31].

An important issue is the precision and the reliability of experimental data and calculations. As most of our rotational assignments were confirmed by ground state combination difference relations, our vibration-rotation levels and band centers can be considered as firmly established with an experimental accuracy of $0.001\text{--}0.01 \text{ cm}^{-1}$. Calculations were done by using two independent methods: variational [17] and algebraic (contact transformations [29]) that permitted a normal mode decomposition of calculated wave functions. We became aware of a recent confirmation [32] of our calculated values using independent adiabatic variational method in hyperspherical coordinates [33] that gives average discrepancies with our values of $\sim 0.01\text{--}0.1 \text{ cm}^{-1}$ for vibrational levels. Consequently, the calculated reef impact up to 30 cm^{-1} in Fig. 4 is a statistically well-determined effect that could be firmly attributed to the shape of the PES in the TS range and not to experimental or calculated uncertainties.

In conclusion, our line-by-line analyses of experimental spectra have evidenced vibration-rotation resonance perturbations through the coupling with 69 “dark” states, each of them inducing the strong mixing of 10–30 rovibrational levels. These results partly confirm Marcus’ proposal [11] concerning the key role of resonances in the dynamics of excited ozone but also prove that internal ozone motion cannot be considered as fully statistical. The latter conclusion is consistent with results of reactive scattering [24] and with the corresponding quantum calculations [23]. Figure 3 illustrates irregular behavior of the normal mode

coupling with increasing energy. The spectroscopic and coupling constants, rovibrational energy levels, and resonance mixing coefficients will be reported elsewhere.

Our comparison of accurate theoretical predictions with a new set of high-resolution spectroscopic data [Table I(a)] obtained via an ultrasensitive CRDS experiment strongly suggests the absence of the submerged barrier at the dissociation ozone channel, making the interpretation of physical and chemical experiments in agreement.

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