3-14-2019

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The ratio of the number of states in asymmetric and symmetric ozone molecules deviates from the statistical value of 2

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ABSTRACT
Accurate calculations of vibrational states in singly and doubly substituted ozone molecules are carried out, up to dissociation threshold. Analysis of these spectra reveals noticeable deviations from the statistical factor of 2 for the ratio between the number of states in asymmetric and symmetric ozone molecules. It is found that, for the lower energy parts of spectra, the ratio is less than 2 in the singly substituted ozone molecules, but it is more than 2 in the doubly substituted ozone molecules. However, the upper parts of spectra, just below dissociation thresholds, exhibit a different behavior. In this energy range, the singly and doubly substituted ozone molecules behave similar, with the ratio of states in asymmetric and symmetric ozone molecules being more than 2 in both cases. This property may contribute to an explanation of the mysterious $\eta$-effect in the ozone forming reaction that favors the formation of the asymmetric ozone molecules.

Mass-independent fractionation of oxygen isotopes in Earth’s atmosphere is produced by recombination reaction that forms ozone molecules: $\text{O} + \text{O}_2 + \text{bath gas} \rightarrow \text{O}_3$. It is known that when rare isotopes of oxygen are involved (e.g., $^{18}\text{O}$), the rate of this reaction is lower by 16% for symmetric ozone molecules, such as $^{16}\text{O}^{18}\text{O}^{16}\text{O}$ and $^{18}\text{O}^{16}\text{O}^{16}\text{O}$, compared to the rate of formation of asymmetric ozone molecules, such as $^{18}\text{O}^{16}\text{O}^{16}\text{O}$ and $^{16}\text{O}^{18}\text{O}^{16}\text{O}$. Interestingly, the magnitude of this effect is the same for both singly and doubly substituted ozone species. The molecular origin of this unusual phenomenon, known as $\eta$-effect, is not yet entirely clear, despite the fact that the earlier theoretical work was rather successful in offering an interpretation of another large mass-dependent isotope effect in ozone, caused by the vibrational zero-point energy change.

The number of states in the products has direct bearing on the reaction rate, and it is usually argued that the number of states in symmetric ozone molecules is a factor of two smaller than in the asymmetric ozone molecules. This difference is rationalized, sometimes, by invoking rotational symmetry numbers for symmetric ozone molecules, but the actual reason for this factor is the doubled phase-space available for vibrations of asymmetric ozone molecules. One can explain this in simple terms, if one notices that among the three possible isomers of isotopically substituted ozone (isotopomers) only one is symmetric, whereas two others are asymmetric, for example, symmetric $^{18}\text{O}^{16}\text{O}^{16}\text{O}$ vs. asymmetric $^{16}\text{O}^{16}\text{O}^{18}\text{O}$ and $^{18}\text{O}^{16}\text{O}^{16}\text{O}$, and similar in the case of double substitution. More rigorous way of looking into this is through the “map” of the potential energy surface (PES) presented in Fig. 1. This diagram shows three deep covalent wells of $\text{O}_3$ connected to three $\text{O} + \text{O}_2$ reaction channels, through the regions of weak van der Waals interaction. One of these wells (in the middle) hosts the symmetric ozone molecule, while two other wells host the asymmetric ozone molecules. Clearly, two wells can support twice larger number of the vibrational states. In the recent thesis and in another recent paper, we carefully worked out what rotational-vibrational states are allowed by symmetry and showed that, indeed, their numbers in the symmetric and asymmetric ozone molecules are in the ratio of one to two, roughly. We also showed that this factor of two, by itself, is not responsible for any isotope effects since it cancels analytically if all features of this reaction are properly taken into account.
Note that the vibrational wave functions of singly and doubly substituted ozone are either symmetric (symmetry $A_1$) or antisymmetric (symmetry $B_1$) with respect to reflection through the dashed line in Fig. 1. This assignment is exact, and, in fact, the states of different symmetries are computed in two independent runs with symmetry-adapted basis sets specified for the hyper-angle $\varphi$. The corresponding states are reported separately: $A_1$ states in Tables S1, S3, S5, and S7 and $B_1$ states in Tables S2, S4, S6, and S8. In addition, we tried our best to split the vibrational states onto the nearly degenerate pairs (that correspond to the double-well states of asymmetric ozone and the double-channel van der Waals states) and the remaining non-degenerate states (that correspond to the single-well symmetric ozone and the single-channel van der Waals states). This degeneracy assignment is approximate but is quite certain for the majority of ozone states. The non-degenerate states are reported in Tables S1, S2, S5, and S6, and the nearly degenerate states are reported in Tables S3, S4, S7, and S8.

Figures 2 and 3 demonstrate energies of the vibrational states in the upper part of spectrum of singly substituted ozone. Similar pictures for the overall energy range and for the case of doubly substituted ozone are given in the supplementary material. At lower energies, in the asymmetric ozone molecule, the states of symmetries $A_1$ and $B_1$ are nearly degenerate (see Fig. 2), just like in a classic double-well problem, while in the spectrum of symmetric
ozonation, the energies of the states of symmetries $A_1$ and $B_1$ alternate (see Fig. 3). However, near dissociation threshold, at energies above $\sim 130 \text{ cm}^{-1}$, the PES opens up toward dissociation channels and the spectrum is significantly modified. The weakly bound van der Waals states dominate in this energy range, but several vibrational states localized in the covalent wells are also present. For this reason, the densities of states in both symmetric and asymmetric ozone molecules increase near threshold, as one can see from Figs. 2 and 3.

Careful analysis of the data in Tables S1–S8 reveals that the vibrational states of covalently bound symmetric and asymmetric ozone isotopomers (pink and orange in Fig. 1) never mix. However, the weakly bound states with dominant van der Waals character (green in Fig. 1) sometimes mix with symmetric (pink) and asymmetric (orange) ozone molecules simultaneously. Such cases, however, are not numerous. They represent exceptions rather than a rule. Overall, one can say that the vibrational states of symmetric and asymmetric ozone molecules are rather independent.

In Fig. 4, we present a comparison of our computed state energies with those reported by Dawes and co-workers, and Poirier and co-workers (available for the singly substituted ozone only) using the same PES. In our calculations, the values of energies converged to $10^{-3} \text{ cm}^{-1}$ for the vibrational states with energies below $4800 \text{ cm}^{-1}$ (about 50 symmetric and 45 antisymmetric states), to $10^{-2} \text{ cm}^{-1}$ in the energy range below $2700 \text{ cm}^{-1}$ (about 150 lowest symmetric and 135 lowest antisymmetric states), and to $10^{-1} \text{ cm}^{-1}$ at higher energies.

As one can see from Fig. 4, our results agree much better with the results of Poirier and co-workers. The differences are on the order of $10^{-3} \text{ cm}^{-1}$, which was the targeted energy convergence in both ours and their calculations. Interestingly, the states of asymmetric ozone $^{16}\text{O}^{18}\text{O}^{16}\text{O}$ obtained by Poirier are systematically closer to our results. On average, they are just $-0.002 \text{ cm}^{-1}$ above our energies. For symmetric ozone $^{16}\text{O}^{16}\text{O}^{16}\text{O}$, the average deviation is larger, about $0.009 \text{ cm}^{-1}$. This feature, most probably, is due to the Jacobi coordinates (employed by Poirier and co-workers) that treat the wells of symmetric and asymmetric ozone unevenly as it was pointed out in their paper. Here, we use the hyper-spherical coordinates that represent all three wells of ozone on equal footing.

The deviations of our predicted energies from those reported by Dawes and co-workers are somewhat larger. The differences start at about $0.1 \text{ cm}^{-1}$ for the ground vibrational state and grow up to the average deviation of $0.7 \text{ cm}^{-1}$ for higher energy states. Surprisingly, for many van der Waals states near the dissociation threshold, the agreement becomes much better (with deviations of the order of $10^{-2} \text{ cm}^{-1}$ for many states, see Fig. 4). Also, we noticed that, when shifted to the same energy origin, all eigenvalues of Poirier are lower than those of Dawes, and ours are even lower than those of Poirier. Figure 4 gives the absolute values (moduli) of the deviations.

In Fig. 5, we present splittings between the nearly degenerate states of symmetries $A_1$ and $B_1$ in the asymmetric ozone molecule $^{18}\text{O}^{16}\text{O}^{16}\text{O}$. Some relevant data available from the literature are also presented, for comparison. The splittings we obtained for several lower vibrational states are on the order of $10^{-8} \text{ cm}^{-1}$, but they increase roughly exponentially with increasing vibrational excitation. One can wonder if these predictions are reliable at all since the values of splitting are so small. We carefully checked all convergence parameters and concluded that the values of those tiny splittings are converged, on average, to 20% of their values. Importantly, Dawes reported that the value of splitting in his calculations was on the order of $10^{-8} \text{ cm}^{-1}$ for the ground state, which is quite similar to our results. Moreover, the values of splittings we found for the van der Waals states in the upper part of spectrum are also in reasonable agreement with the data of Dawes (see Fig. 5).

Energies of vibrational states of ozone, $E_\nu$, reported in Tables S1–S8, can be used to compute the following averaged

![FIG. 3. The spectrum of non-degenerate states of symmetric ozone molecule near dissociation threshold. Blue and red dots represent the covalently bound vibrational states of two symmetries, $A_1$ and $B_1$, respectively. Green and black dots mark the van der Waals states of vibrational symmetries $A_2$ and $B_2$, respectively. State numbering is according to Tables S1 and S2 of the supplementary material.](image-url)

![FIG. 4. Comparison of the computed state energies (horizontal) with the results of Dawes and Poirier. The vertical axis shows the modulus of deviation. Green and gray circles correspond to vibrational states of symmetries $A_1$ and $B_1$ from Ref. 23. Blue and red symbols correspond to Ref. 20.](image-url)
difference between $Q_{\text{sym}}$ and $Q_{\text{asym}}$, both red and orange wells of the PES in Fig. 1 (i.e., contributes roughly the same amount of energy to the vibrational states of ozone bound in the covalent wells and to the vibrational states of ozone bound in the covalent wells). The expected statistical value of two is indicated by the dashed line. The deviations of computed data from this reference are obvious in a broad range of energies. Asymptotically they reach roughly $\pm 0.05$.

In Fig. 6, we report the ratio of the average number of states in asymmetric and symmetric ozone molecules, as defined by Eq. (1). Blue and red curves correspond to singly and doubly substituted ozone. The horizontal axis gives the averaging energy window size $\Delta E$, which in this case is analogous to the thermal energy in the vibrational partition function. The statistical value of two is indicated by the dashed line. The deviations of computed data from this reference are obvious in a broad range of energies. Asymptotically they reach roughly $\pm 0.05$.
In Fig. 7, we report the ratio of the average number of states in asymmetric and symmetric ozone molecules, computed as \( R_{\text{dwn}} = \frac{Q_{\text{dwn}}}{Q_{\text{up}}} \), using Eq. (2), for both singly and doubly substituted ozone and plotted versus \( -\Delta E \) in a broad range. The limiting values of \( R_{\text{dwn}} \) for large \( -\Delta E \) match those of \( R_{\text{up}} \) in Fig. 6, roughly \( 2.00 \pm 0.05 \), as one might expect, since in the limit of large \( -\Delta E \) both \( R_{\text{up}} \) and \( R_{\text{dwn}} \) reflect just the total number of states. Moreover, when the value of \( -\Delta E \) is reduced to about \( -\Delta E \sim 100 \text{ cm}^{-1} \), the values of \( R_{\text{dwn}} \) for singly and doubly substituted molecules split even further apart, reaching \( 2.00 \pm 0.20 \) (i.e., 20% difference; see Fig. 7). These numbers indicate a very significant difference between symmetric and asymmetric ozone molecules that has never been noticed before.

Unfortunately, this property does not help to explain the \( \eta \)-effect because our data clearly indicate that singly and doubly substituted molecules behave in the opposite ways, namely, in the singly substituted case, the symmetric ozone molecule exhibits more states than expected, whereas in the doubly substituted case, the asymmetric ozone molecule exhibits more states than expected.

However, at small values of \( -\Delta E \), the behavior of two \( R_{\text{dwn}}(\Delta E) \) dependencies drastically change. We see from Fig. 7 that in the energy range \( -\Delta E < 20 \text{ cm}^{-1} \), the values of \( R_{\text{dwn}} \) for singly and doubly substituted ozone molecules approach each other, and both exceed the value of 2.00, substantially. This happens because for small values of \( -\Delta E \) only the very top portion of the spectrum is available, where the ratio of the number of states between asymmetric and symmetric ozone molecules is similar in both singly and doubly substituted cases. This holds true only at the very top of the spectrum, so, as \( -\Delta E \) increases and more states become available, the main trend, observed in Fig. 6, starts to dominate again and the curves return to the same asymptotic values.

Although the behavior of \( R_{\text{dwn}} \) in the range of small \( -\Delta E \) is potentially important for explanation of the \( \eta \)-effect, it should be stated that this phenomenon is not particularly robust with respect to the variations of theory. For example, we tried to alter (artificially) the values of dissociation thresholds, by few wavenumbers, and found that such modifications may change the low-\( \Delta E \) behavior of \( R_{\text{dwn}} \) seen in Fig. 7. Indeed, the upper part of the spectra contains many delocalized van der Waals states but only a few vibrational states that are localized in the covalent wells of symmetric and asymmetric isotopomers. Thus, addition or removal of just one vibrational state in this energy range may have a significant effect. Such alternation can be caused by small changes of the potential energy surface, by rotational excitation of the molecule, or by involvement of scattering resonances above dissociation threshold (not considered here). All we can say at this time is that for the PES at hands and with the spectra we have accurately computed, the intriguing low-\( \Delta E \) behavior of \( R_{\text{dwn}} \) seen in Fig. 7 is obtained and is potentially important.

It is also debatable whether the van der Waals states of ozone are important for the recombination process or not. Even if the van der Waals complexes of ozone are formed, they are easily destroyed by collisions with bath gas and are hard to stabilize into the main (covalent) well,\(^\text{22}\) where the stable ozone molecules are eventually formed. Therefore, it was argued in the past that these states could be neglected. Here, for the exploratory purpose, we tried to include the van der Waals states into the overall state count, but with the reduced weights of only 10% (which, of course, is rather arbitrary) of their corresponding probabilities \( p_i \) given in the Tables, in order to reflect their weak collisional coupling to the rest of the ozone states. With this scaling factor, we counted the van der Waals states in the average \( Q_{\text{dwn}} \) by (a) associating with asymmetric ozone molecule the probabilities from the “blue” van der Waals part of the map in Fig. 1 and by (b) splitting between symmetric and asymmetric ozone molecules the probabilities from the “green” van der Waals part of the map. The corresponding results are indicated by colored areas in Fig. 7. We can see that in the range of small \( -\Delta E < 20 \text{ cm}^{-1} \), these areas overlap (pink and blue), again, indicating the same behavior of the singly and doubly substituted ozone molecules. Thus, inclusion of the van der Waals states is unlikely to change conclusions of the previous paragraph.

These unexpected properties of the vibrational states spectra in ozone molecules may help to identify possible source of the mysterious \( \eta \)-effect. One very strange feature of the \( \eta \)-effect is that it has the same direction and magnitude in both singly and doubly substituted ozone. In both cases, the asymmetric ozone molecules are formed faster. This is incomprehensible because symmetric and asymmetric isotopomers of ozone behave differently in the singly and doubly substituted cases. For example, in the case of single substitution, the spectrum of asymmetric ozone is shifted up relative to the spectrum of symmetric ozone by \( \Delta ZP\text{E} \) (roughly 10-20 cm\(^{-1}\)), while it is just opposite in the case of the double substitution (see Tables S1–S8). Moreover, the vibrational partition functions ratios, both \( R_{\text{up}} \) and \( R_{\text{dwn}} \), deviate down from the statistical factor of 2 in the case of single substitution (up to \( -10\% \)), while it is just opposite in the case of the double substitution (up to \( +10\% \), see Figs. 6 and 7). These are very robust indications of different behavior of symmetric and asymmetric ozone molecules in the cases of single and double substitutions, yet, the experimental \( \eta \)-effect is the same! Note that beyond
ozone, the symmetry-driven mass-independent isotope effects have been reported for CO$_2$ and SiO$_2$, and may also play some role in the sulfur bearing molecules such as SO$_2$, S$_3$, and S$_4$.

Another new property reported here, which may contribute to an explanation of the $\eta$-effect, is the behavior of the upper parts of the vibrational spectra, just below the dissociation threshold. It appears that in this energy range, the asymmetric ozone molecules contain more than twice as many states than the symmetric ozone molecules, and this property seems to hold for both singly and doubly substituted cases. It should be taken into consideration that the experimental value of energy transfer in ozone is close to $-\Delta E \sim 20$ cm$^{-1}$. Thus, the process of ozone formation must be very sensitive to the properties of this narrow part of the vibrational spectrum. Accurate incorporation of this effect into the models of ozone forming recombination reaction is possible through the rate coefficient $k_{\text{stab}}$ for stabilization of scattering resonances, but this requires calculations of the energy-transfer process, and those are numerically demanding, if at all affordable at present time. However, the findings of this communication may help to develop a practical approximation for the energy-transfer process that still captures this effect.

See supplementary material for a detailed description of technical aspects of our calculations and for the data tables of the vibrational states’ spectra computed in this work for symmetric and asymmetric isotopomers of singly and doubly substituted ozone molecules and the figures of these spectra in the entire energy range and near the dissociation threshold.

This research was supported by the NSF Atmospheric Chemistry Program, Division of Atmospheric Sciences, Grant No. AGS-1252486. This research used resources of the National Energy Research Scientific Computing Center, which is supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

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