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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

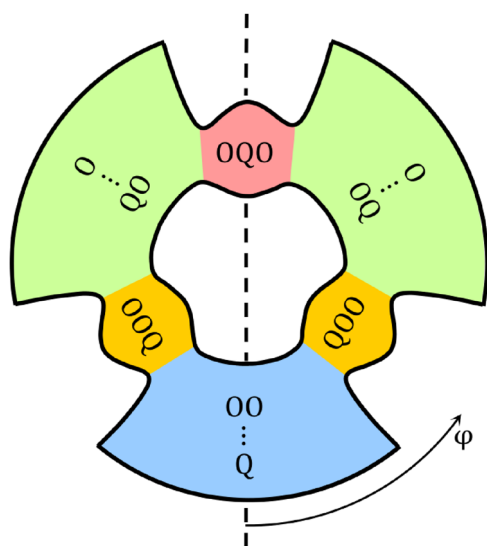
Accurate calculations of vibrational states in singly and doubly substituted ozone molecules are carried out, up to dissociation threshold. Analysis of these spectra reveals noticeable deviations from the statistical factor of 2 for the ratio between the number of states in asymmetric and symmetric ozone 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.

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Mass-independent fractionation of oxygen isotopes in Earth's atmosphere<sup>1,2</sup> is produced by recombination reaction that forms ozone molecules:  $\text{O} + \text{O}_2 \xrightarrow{\text{+bath gas}} \text{O}_3$ . It is known that when rare isotopes of oxygen are involved (e.g., <sup>18</sup>O), the rate of this reaction is lower by 16% for symmetric ozone molecules,<sup>3,4</sup> such as <sup>16</sup>O<sup>18</sup>O<sup>16</sup>O and <sup>18</sup>O<sup>16</sup>O<sup>18</sup>O, compared to the rate of formation of asymmetric ozone molecules, such as <sup>18</sup>O<sup>16</sup>O<sup>16</sup>O and <sup>16</sup>O<sup>18</sup>O<sup>18</sup>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,<sup>5-8</sup> 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.<sup>5,6,9-13</sup>

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 <sup>16</sup>O<sup>18</sup>O<sup>16</sup>O vs. asymmetric <sup>16</sup>O<sup>16</sup>O<sup>18</sup>O and <sup>18</sup>O<sup>16</sup>O<sup>16</sup>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 O<sub>3</sub> connected to three O + O<sub>2</sub> 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<sup>14</sup> and in another recent paper,<sup>15</sup> 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.<sup>15</sup>



**FIG. 1.** A map of the PES of ozone in the hyper-spherical coordinates. O and Q denote two different oxygen isotopes, such as  $^{16}\text{O}$  and  $^{18}\text{O}$ . Three potential energy wells (pink, orange) connect through three weak van der Waals interaction regions (green, blue). Note that asymmetric ozone molecules occupy two potential wells (orange), whereas symmetric ozone molecules occupy only one (pink).

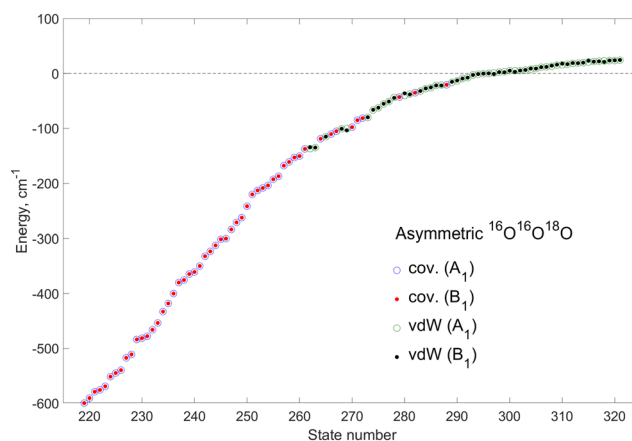
But what if this difference is not exactly a factor of two? What if the ratio of the actual number of vibrational states deviates from this statistically driven expectation? Surprisingly, the literature search on this topic reveals that although several accurate PESs exist for ozone<sup>9,16–18</sup> and several calculations of its vibrational spectra have been reported,<sup>19–23</sup> no one tried to compare the number of states in symmetric and asymmetric ozone molecules systematically, for both singly and doubly substituted cases. Here we report such data, obtained by accurate variational calculations of the vibrational states and determine the ratio of the corresponding vibrational partition functions for the relevant isotopomers of ozone. Our results indicate a non-negligible deviation from the factor of two and, thus, attest for an appreciable isotope effect. To our best knowledge, this property of the ozone molecule has never been noticed before. In what follows, we present and analyze the results of two sets of calculations. One set is for the singly substituted ozone ( $^{18}\text{O}^{16}\text{O}^{16}\text{O}$  and  $^{16}\text{O}^{18}\text{O}^{16}\text{O}$  molecules) that corresponds to the excess of  $^{16}\text{O}$  with a trace amount of  $^{18}\text{O}$ . The second set is for the doubly substituted ozone ( $^{18}\text{O}^{18}\text{O}^{16}\text{O}$  and  $^{18}\text{O}^{16}\text{O}^{18}\text{O}$  molecules) that corresponds to the excess of  $^{18}\text{O}$  with trace amounts of  $^{16}\text{O}$ .

Calculations reported here were carried out using the adiabatically-adjusting principal axis hyperspherical (APH) coordinates<sup>24</sup> ( $\rho$ ,  $\theta$ ,  $\varphi$ ) in the entire range of the hyper-angle  $\varphi$  that covers all three wells of Fig. 1. This means that the vibrational states of both symmetric and asymmetric ozone isotopomers are computed at once and must be assigned and split onto the groups afterwards. In order to do these assignments, we computed, for each vibrational wave function, four probabilities associated with colored regions of the coordinate space in Fig. 1. Two of these probabilities correspond to the regions of deep covalent wells ( $\rho < 5$  bohrs), and the other two

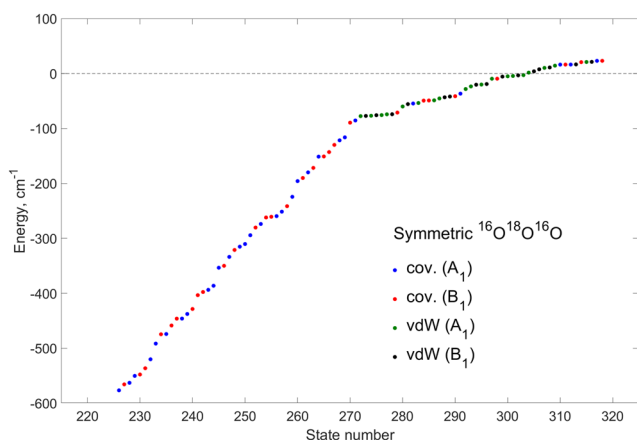
correspond to the regions of shallow van der Waals wells ( $5 < \rho < 11$  bohrs). For example, in the case of single isotopic substitution, the four probabilities correspond to symmetric ozone  $^{16}\text{O}^{18}\text{O}^{16}\text{O}$ , asymmetric ozone  $^{18}\text{O}^{16}\text{O}^{16}\text{O}$  and  $^{16}\text{O}^{16}\text{O}^{18}\text{O}$  (the two wells combined), van der Waals complex  $^{16}\text{O}^{16}\text{O}\cdots^{18}\text{O}$ , and finally the  $^{18}\text{O}^{16}\text{O}\cdots^{16}\text{O}$  van der Waals complex (in the two channels combined, see Fig. 1). These four probabilities are listed for each vibrational state of ozone in the Tables S1–S8 of the [supplementary material](#). Tables S1–S4 report the data for ozone with single  $^{18}\text{O}$ , while Tables S5–S8 report the data for double substitutions with  $^{18}\text{O}$ .

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



**FIG. 2.** The spectrum of nearly degenerate states of asymmetric ozone molecule close to dissociation threshold. Blue circles and red dots represent the covalently bound vibrational states of two symmetries,  $A_1$  and  $B_1$ , respectively. Green circles and black dots mark the van der Waals states of vibrational symmetries  $A_1$  and  $B_1$ , respectively. State numbering is according to Tables S3 and S4 of the [supplementary material](#).



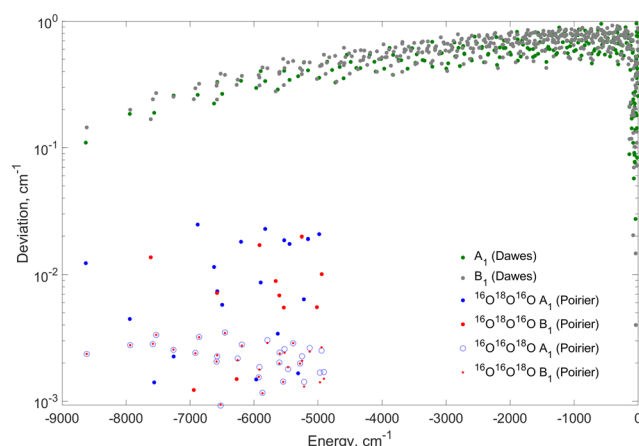
**FIG. 3.** The spectrum of non-degenerate states of symmetric ozone molecule near dissociation threshold. Blue and red dots represent the covalently bound vibrational states of two symmetries,  $A_1$  and  $B_1$ , respectively. Green and black dots mark the van der Waals states of vibrational symmetries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

ozone, the energies of the states of symmetries  $A_1$  and  $B_1$  alternate (see Fig. 3). However, near dissociation threshold, at energies above  $-130 \text{ cm}^{-1}$ , 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<sup>20</sup> and Poirier and co-workers<sup>23</sup> (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.<sup>23</sup> Interestingly, the states of asymmetric ozone  $^{18}\text{O}^{16}\text{O}^{16}\text{O}$  obtained by Poirier are systematically closer to our results. On average, they are just  $\sim 0.002 \text{ cm}^{-1}$  above our energies. For symmetric ozone  $^{16}\text{O}^{18}\text{O}^{16}\text{O}$ , the average deviation is larger, about  $0.009 \text{ cm}^{-1}$ . This feature, most probably, is due



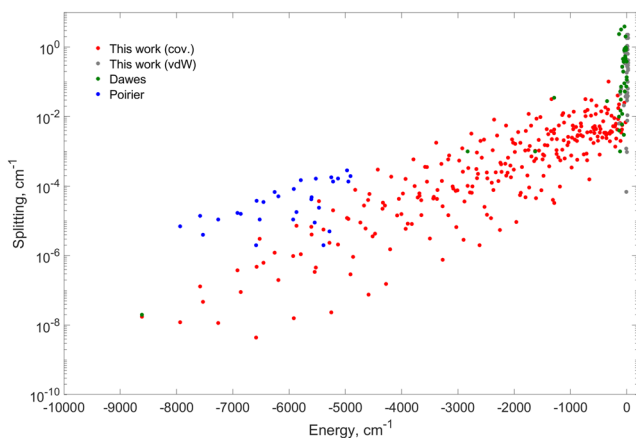
**FIG. 4.** Comparison of the computed state energies (horizontal) with the results of Dawes<sup>20</sup> and Poirier.<sup>23</sup> The vertical axis shows the modulus of deviation. Green and gray circles correspond to vibrational states of symmetries  $A_1$  and  $B_1$  from Ref. 20. Blue and red symbols correspond to Ref. 23 as follows: filled blue and red circles correspond to the vibrational states of symmetries  $A_1$  and  $B_1$ , respectively, in symmetric ozone molecule; empty blue circles and small red dots correspond to symmetries  $A_1$  and  $B_1$  of asymmetric ozone molecule.

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.<sup>23</sup> 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<sup>20</sup> 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,<sup>20</sup> 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<sup>20</sup> (see Fig. 5).

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



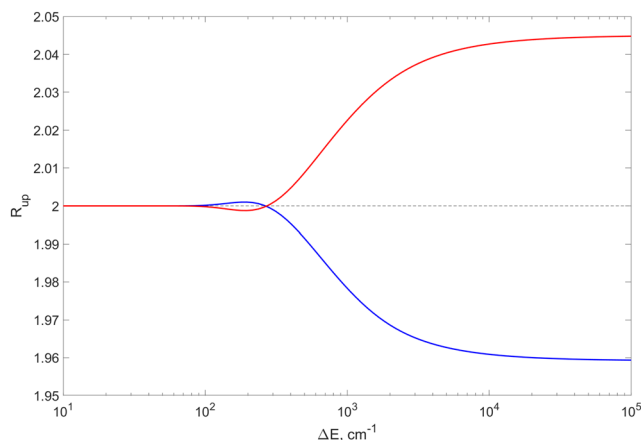
**FIG. 5.** Splittings of the nearly degenerate vibrational states of asymmetric ozone molecule, as a function of state energy. Red and gray dots correspond to the covalently bound vibrational states and the weakly bound van der Waals states, respectively, computed in this work. Green and blue dots show results available from Refs. 20 and 23, respectively.

characteristics for the spectra of symmetric and asymmetric ozone molecules,

$$Q_{\text{up}}(\Delta E) = \sum_i p_i \exp\left\{-\frac{E_i - E_0}{\Delta E}\right\}. \quad (1)$$

This moiety is very similar to the vibrational partition function where thermal energy is replaced by a continuous positive variable  $\Delta E$  measured here in wavenumbers. Summation is over all states including two vibrational symmetries ( $A_1$  and  $B_1$ ) but is done differently for symmetric and asymmetric ozone molecules. Namely, when Eq. (1) is used to compute  $Q_{\text{up}}^{\text{sym}}$  and  $Q_{\text{up}}^{\text{asym}}$ , the corresponding probabilities are invoked,  $p_i^{\text{sym}}$  and  $p_i^{\text{asym}}$ , respectively. These are taken from Tables S1–S8 and are introduced to handle those rare cases when the vibrational wave function is delocalized over both red and orange wells of the PES in Fig. 1 (i.e., contributes to both symmetric and asymmetric ozone molecules). The second difference between  $Q_{\text{up}}^{\text{sym}}$  and  $Q_{\text{up}}^{\text{asym}}$  is the origin of their spectra—the ground state energy  $E_0$ . From the tables, one can see that for singly substituted ozone, the ground state of asymmetric  $^{18}\text{O}^{16}\text{O}^{16}\text{O}$  is  $14.250 \text{ cm}^{-1}$  above the ground state of symmetric  $^{16}\text{O}^{18}\text{O}^{16}\text{O}$ . In the doubly substituted case, the order is reversed: the ground state of symmetric  $^{18}\text{O}^{16}\text{O}^{18}\text{O}$  is  $14.494 \text{ cm}^{-1}$  above the ground state of the asymmetric  $^{16}\text{O}^{18}\text{O}^{18}\text{O}$ .

In Fig. 6, we report the ratio of the average number of energetically available states in asymmetric and symmetric ozone molecules, computed as  $R_{\text{up}} = Q_{\text{up}}^{\text{asym}}/Q_{\text{up}}^{\text{sym}}$  for both singly and doubly substituted ozone, plotted as a function of the variable  $\Delta E$  in a broad range. The expected statistical value of this ratio is two, but our data agree with this number only if the value of  $\Delta E$  is small, below  $70 \text{ cm}^{-1}$ . Note that the vibrational quanta of ozone near the bottom of the well are on the order of  $700 \text{ cm}^{-1}$ . We see that for  $\Delta E \sim 700 \text{ cm}^{-1}$ , the value of  $R_{\text{up}}$  for the singly substituted ozone is clearly below two, while for the doubly substituted ozone, it is clearly above two. For  $\Delta E \sim 7000 \text{ cm}^{-1}$ , when the upper vibrational states near threshold start contributing into  $Q_{\text{up}}$ , the deviations from 2.00 approach  $\pm 0.05$  roughly (more precisely,  $-0.0406$  for the singly



**FIG. 6.** 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  $\pm 0.05$ .

substituted ozone and  $+0.0448$  for the doubly substituted ozone). So, both singly and doubly substituted ozone deviate significantly from the expected factor of two, but these deviations occur in the opposite directions. It is important to emphasize that these effects occur due to the vibrational states of ozone bound in the covalent wells and thus are robust. Any reasonable calculations of the vibrational states of ozone should be able to reproduce this unusual property.

It is rather clear that  $Q_{\text{up}}$  of Eq. (1) gives preference to the low-energy states, near the bottom of the covalent well on the PES, just as the usual vibrational partition function. In order to characterize properties of the upper parts of the spectra, we tried to compute

$$Q_{\text{down}}(\Delta E) = \sum_i p_i \exp\left\{-\frac{E_i - E^*}{\Delta E}\right\}, \quad (2)$$

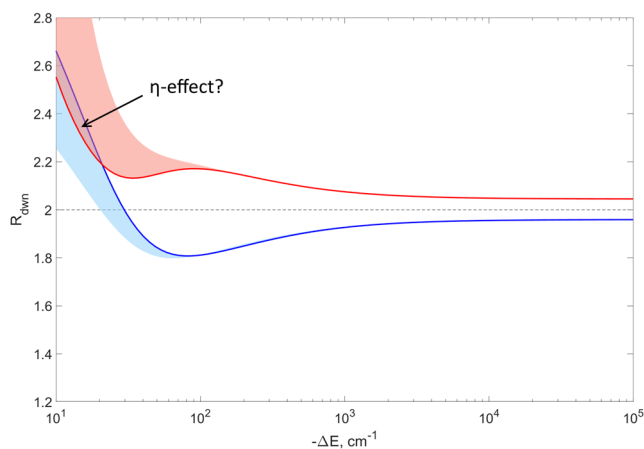
where  $E^*$  is the dissociation threshold and  $\Delta E$  is negative. Upper vibrational states, just below the threshold, are more important for the process of ozone formation since the scattering resonances above threshold (the metastable ozone states) are stabilized into the upper bound states by the bath gas collisions. The energy transfer process is typically exponential, so the sum of Eq. (2) is expected to reflect the total stabilization probability (besides giving the average number of states near threshold). Thus,  $\Delta E$  can be thought of as the average amount of transferred energy. The values of threshold energies  $E^*$  are defined based on zero-point energies of  $^{16}\text{O}^{16}\text{O}$ ,  $^{16}\text{O}^{18}\text{O}$ , and  $^{18}\text{O}^{18}\text{O}$  in the corresponding dissociation/reaction channels.<sup>10,11</sup> Zero energy always corresponds to the lowest dissociation threshold. Thus, in the case of single substitution, the threshold for asymmetric  $^{18}\text{O}^{16}\text{O}^{16}\text{O}$  is  $25.141 \text{ cm}^{-1}$  above the threshold for the symmetric  $^{16}\text{O}^{18}\text{O}^{16}\text{O}$ , which represents zero-point energy change between  $^{16}\text{O}^{16}\text{O}$  and  $^{16}\text{O}^{18}\text{O}$ . In the case of double substitution, the order is opposite: the threshold for symmetric  $^{18}\text{O}^{16}\text{O}^{18}\text{O}$  is  $20.385 \text{ cm}^{-1}$  above the threshold for asymmetric  $^{16}\text{O}^{18}\text{O}^{18}\text{O}$ , which represents zero-point energy change between  $^{16}\text{O}^{18}\text{O}$  and  $^{18}\text{O}^{18}\text{O}$ .



In Fig. 7, we report the ratio of the average number of states in asymmetric and symmetric ozone molecules, computed as  $R_{\text{down}} = Q_{\text{down}}^{\text{asym}}/Q_{\text{down}}^{\text{sym}}$  using Eq. (2), for both singly and doubly substituted ozone and plotted versus  $-\Delta E$  in a broad range. The limiting values of  $R_{\text{down}}$  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  $I_{\text{down}}$  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  $R_{\text{down}}$  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  $R_{\text{down}}(\Delta E)$  dependencies drastically change. We see from Fig. 7 that in the energy range  $-\Delta E < 20 \text{ cm}^{-1}$ , the values of  $R_{\text{down}}$  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.



**FIG. 7.** Ratio of the average number of states in asymmetric and symmetric ozone molecules, as defined by Eq. (2). 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 vibrational energy transfer due to bath gas collisions. The statistical value of two is indicated by the dashed line. The deviations of computed data from this reference increase at low energies, reaching  $\pm 0.20$ , and then merge near  $-\Delta E \sim 20 \text{ cm}^{-1}$ , indicating a possible source of  $\eta$ -effect.

Although the behavior of  $R_{\text{down}}$  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  $R_{\text{down}}$  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  $R_{\text{down}}$  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,<sup>25</sup> 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  $Q_{\text{down}}$  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  $\Delta ZPE$  (roughly  $10\text{--}20 \text{ cm}^{-1}$ ), 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  $R_{\text{down}}$ , 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<sub>2</sub> and SiO<sub>2</sub><sup>26,27</sup> and may also play some role in the sulfur bearing molecules such as SO<sub>2</sub>, S<sub>3</sub>, and S<sub>4</sub>.<sup>28,29</sup>

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<sup>30</sup> is expected to be close to  $-\Delta E \sim 20 \text{ cm}^{-1}$ . 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<sup>13</sup> 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.

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