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# Surprising rate coefficients for four isotopic variants of $O+O_2+M$

S. M. Anderson,<sup>a)</sup> Detlev Hülsebusch, and Konrad Mauersberger

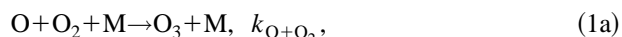
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Mass spectrometric analysis of nonequilibrium oxygen isotopic mixtures undergoing UV photolysis has been employed to study three-body recombination rate coefficients for the  $O+O_2$ ,  $Q+O_2$ ,  $O+Q_2$ , and  $Q+Q_2$  ( $O=^{16}O$ ,  $Q=^{18}O$ ) reactions, all with  $M=80\% N_2:10\% O_2:10\% Q_2$  at 200 Torr and 296 K.  $k_{O+O_2}$  is in good agreement with the currently recommended value, while  $k_{Q+Q_2}$  is only slightly smaller. Surprisingly,  $k_{Q+O_2}$  is close to  $k_{O+O_2}$ , while  $k_{O+Q_2}$  is  $\approx 50\%$  larger. As a consequence of this unusual behavior,  $k_{O+OQ}$  must be  $\approx 20\%$  larger than  $k_{Q+OQ}$  to produce the well-known enrichments that occur in the free atmosphere and in laboratory experiments involving scrambled mixtures. Contrary to what is usually assumed in discussions of the heavy ozone anomaly, these results indicate that isotopic asymmetry does *not* guarantee a rate coefficient advantage. © 1997 American Institute of Physics. [S0021-9606(97)02038-2]

## I. INTRODUCTION

The Chapman reaction by which nearly all ozone in the Earth's atmosphere is formed,



exhibits a number of peculiar properties. Perhaps the most difficult to understand are the anomalous abundances of isotopically labeled ozone produced by isotopic variants of this reaction.<sup>1</sup> The physical reason for these anomalies remains unknown despite considerable investigation,<sup>2-5</sup> although models that do not involve recombination<sup>6,7</sup> have largely been eliminated by successively "cleaner" laboratory experiments.<sup>1,5</sup> A mechanism based on reaction (1), but involving either modifications of conventional recombination theory<sup>8-10</sup> or the formation of electronically excited ozone during  $O+O_2$  collisions,<sup>11,12</sup> appears to be necessary.

All such models assume that isotopic asymmetry, in either the newly formed atom-diatom collision pair or the diatom alone, plays a central role in producing a rate coefficient advantage. This assertion was initially motivated by the apparent insensitivity of the enrichments to substituent mass,<sup>2</sup> and further supported by experiments capable of separately detecting the symmetric (OQO) and asymmetric (QO<sub>2</sub>) isotopomers.<sup>13</sup> That such qualitative, symmetry-controlled effects are well-known in molecular spectroscopy has lent credence to this asymmetry-advantage assumption, yet it has never been fully tested due to the difficulty of isolating the desired isotopic variants of the reaction. When ozone is generated from isotopically scrambled material, asymmetric molecules are produced by more than one reaction; i.e., QO<sub>2</sub> from  $Q+O_2$  as well as QO+O. The problem is compounded when products are detected without symmetry specificity and made insoluble when ozone is converted to molecular oxygen prior to isotopic analysis.

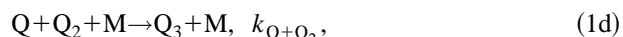
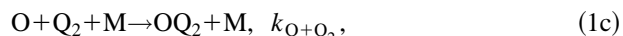
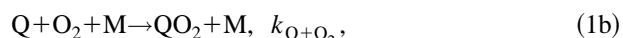
A first step towards testing the asymmetry-advantage hypothesis was taken recently by Sehested *et al.*,<sup>3</sup> who com-

bined pulsed radiolysis of four well-chosen isotopic mixtures with time-resolved detection of total ozone via UV absorption to determine rate coefficients for certain groups of reactions. From these they derived rate coefficients for  $O+O_2$ ,  $Q+Q_2$ , the average of  $Q+O_2$  and  $O+Q_2$ , and the average of  $O+OQ$  and  $Q+OQ$ , all for  $M=CO_2$  at 1 bar (760 Torr) total pressure. The results were not as clear as one might have hoped if symmetry was indeed playing a central role.

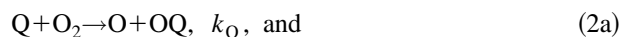
In this work, we have taken another step by fully isolating four isotopic variants of reaction (1), namely  $O+O_2$ ,  $Q+O_2$ ,  $O+Q_2$ , and  $Q+Q_2$ . In the context of Sehested *et al.*'s study our primary contribution is the separation of  $Q+O_2$  from  $O+Q_2$ . This turns out to be of fundamental importance.

## II. THEORY

The presence of oxygen atoms in a system containing  $O_2$ ,  $Q_2$ , and  $M$  (but without OQ) will lead to the following reactions in addition to (1a):



as well as the exchange reactions:



Previous work has indicated that the products of reactions (1b) and (1c) are as indicated,<sup>14,15</sup> though this fact is not critical for the present work. Reactions (2) determine the steady-state  $[Q]/[O]$  ratio and catalytically produce OQ.

The following ozone rate equations apply if reactions (1) are the only significant processes affecting ozone concentrations:

$$d[O_3]/dt = k_{O+O_2}[O][O_2][M], \quad (3a)$$

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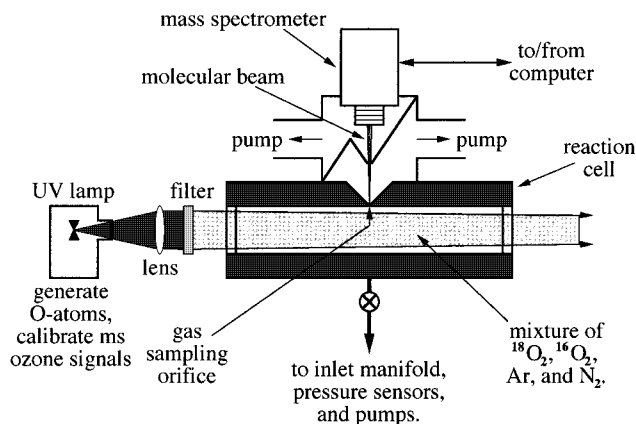


FIG. 1. Schematic diagram of the apparatus used in this work.

$$d[\text{QO}_2]/dt = k_{\text{Q}+\text{O}_2}[\text{Q}][\text{O}_2][\text{M}], \quad (3b)$$

$$d[\text{OO}_2]/dt = k_{\text{O}+\text{Q}_2}[\text{O}][\text{Q}_2][\text{M}], \quad (3c)$$

$$d[\text{Q}_3]/dt = k_{\text{Q}+\text{Q}_2}[\text{Q}][\text{Q}_2][\text{M}]. \quad (3d)$$

The concentration of each ozone isotopomer grows linearly with time if reactant concentrations are fixed, and the various ozone concentrations are proportional to their respective rate coefficients. The concentration of OQ varies according to:

$$d[\text{OQ}]/dt = k_{\text{Q}}[\text{Q}][\text{O}_2] + k_{\text{O}}[\text{O}][\text{Q}_2], \quad (4)$$

such that [OQ] also increases linearly with time. The rate of OQ production can therefore be employed to determine atom number densities, and we have exploited this fact to put our rate coefficients on an absolute scale.

Equations (3) show that, apart from a factor depending only on the *molecular* composition of the mixture, ratios of concentration intervals involving the same atomic species, such as  $d[\text{OO}_2]/d[\text{O}_3]$ , yield ratios of rate coefficients directly; i.e.,  $k_{\text{O}+\text{Q}_2}/k_{\text{O}+\text{O}_2}$ . Interpretation of other interval ratios, such as  $d[\text{Q}_3]/d[\text{O}_3]$ , also requires knowledge of the partitioning of atoms between O and Q, which is controlled by the exchange reactions (2) and ultimately depends on the ratio  $k_{\text{Q}}/k_{\text{O}}$ . The ratio of exchange rate coefficients can be estimated from fundamental reaction rate theory (Appendix A) or from the isotopic enrichments of Q<sub>3</sub> observed in scrambled mixtures (Sec. V). These approaches produce rather different results (1.156 versus 1.245), but the impact of this uncertainty on the principal conclusions of this paper is minimal.

### III. EXPERIMENT

The apparatus (Fig. 1) was designed to allow us to approach the ideal conditions just discussed. N<sub>2</sub>:O<sub>2</sub>:Q<sub>2</sub> mixtures were prepared manometrically in a UHV gas handling system equipped with MKS Baratron pressure sensors. Q<sub>2</sub> (Isotec, 99.3 atom %) was further purified by slow passage through a liquid nitrogen-cooled trap to remove traces of water and carbon dioxide. Q-depleted O<sub>2</sub> (Isotec, O<sub>2</sub>/OQ ≈ 7000) and research grade N<sub>2</sub> (99.9999%) were used

without further purification. For this work the N<sub>2</sub>:O<sub>2</sub>:Q<sub>2</sub> composition was 80:10:10. Premixed gases were admitted to the aluminum cell at a pressure near 200 Torr and photolyzed for a few minutes with a collimated and filtered beam from a deuterium lamp (180 ± 5 nm) to generate ground state O and Q atoms. The optical path outside the cell was purged with N<sub>2</sub>. Ozone and OQ concentrations in the cell (20 cm long, 2.54 cm dia., volume ≈ 100 cm<sup>3</sup>) were monitored with a molecular beam mass spectrometer gas analyzer (MBMS),<sup>16</sup> which removed gas slowly from the cell (≈ 1%/min) through a 12.5 μm diameter platinum aperture.

Due to the rapidity of the exchange reactions relative to recombination under these conditions ( $\tau_{\text{ex}} \approx 5 \times 10^{-7}$  s,  $\tau_{\text{rec}} \approx 1 \times 10^{-3}$  s), the photochemical system has no memory of where the oxygen atoms came from. As mentioned above, partitioning of the atoms between O and Q is determined solely by the molecular oxygen concentrations and the ratio of the exchange reaction rate coefficients. The relative photolysis rates of O<sub>2</sub> and Q<sub>2</sub>, for example, play no role in this partitioning. The time scales for transport in the cell are much longer than the chemical time scales (≈ 1.1 and ≈ 70 s for radial and axial diffusion, respectively), so that wall effects should be negligible.

The MBMS analyzer was calibrated for O<sub>3</sub> (or Q<sub>3</sub>) by simultaneously monitoring UV absorption near 254 nm and the MBMS signal at 48 (or 54) amu during photolysis of mixtures containing natural oxygen (or Q<sub>2</sub>) in N<sub>2</sub>. Relatively broadband filters [10 nm full width at half maximum (FWHM)] were employed to reduce the sensitivity of the UV measurements to local vibrational structure in the Hartley band absorption spectrum, and the average cross sections for O<sub>3</sub> (Ref. 17) and Q<sub>3</sub> were assumed to be identical. The small corrections for the number of ozone molecules detected by absorption, but not by the MBMS (i.e., OQO), were applied. OQ sensitivities were determined from 34 amu signals during the O<sub>3</sub> calibrations assuming a natural abundance of OQ in the calibration gas.

Ozone wall loss lifetimes in the cell were several hours. From our peak ozone concentrations of ≈ 10<sup>14</sup> cm<sup>-3</sup> and the measured spectral distribution of the photolysis source, we concluded that secondary processes associated with primary production of O(<sup>1</sup>D) or photolysis of ozone were negligible and that reactions (1) indeed dominated the ozone concentrations.

### IV. RESULTS

Two types of experiments were carried out. The first were simple, qualitative tests focusing on the relative amounts of isotopomers that were produced. As mentioned above, one obtains certain ratios of rate coefficients in a straightforward way from such data. The objective of the second, quantitative, type of experiment was to determine absolute rate coefficients as precisely as possible for each of the four reactions (1a)–(1d).

In the qualitative experiments the N<sub>2</sub>:O<sub>2</sub>:Q<sub>2</sub> ≈ 80:10:10 mixture was admitted to the cell continuously to maintain the total pressure in the cell. Mass spectra of the ozone peaks

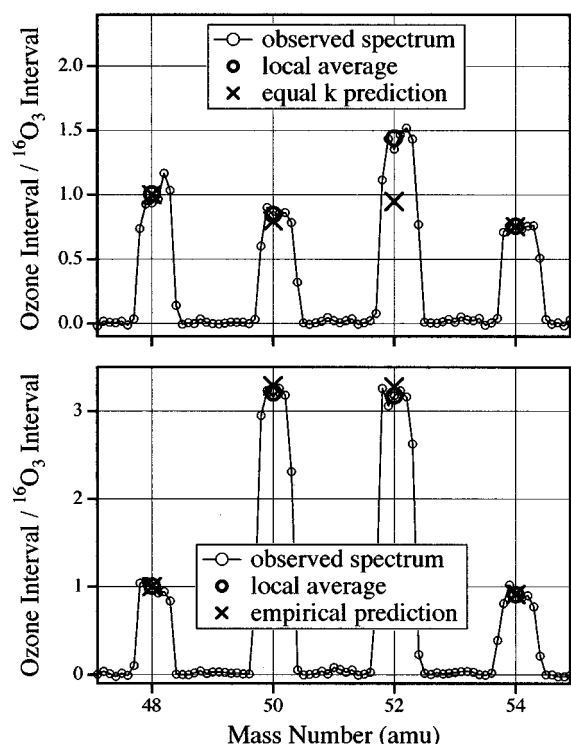


FIG. 2. Intervals of ozone isotopomers (normalized to  $d[\text{O}_3]$ ) produced in 80:10:10 mixtures of  $\text{N}_2:\text{Q}_2:\text{O}_2$ . Unscrambled mixture in upper panel (a), scrambled mixture in lower panel (b). Heavy circles represent the average of data points near the top of each mass peak. See text regarding predicted values (heavy crosses).

were recorded before and after 5 min of photolysis. The difference between these yields a spectrum representing the ozone that was created during the photolysis period, i.e.,  $d[\text{O}_3]$ , etc.. Note that the lack of OQ in the mixture ( $[\text{Q}_2] \approx [\text{O}_2] \gg [\text{OQ}]$  holds even after photolysis) means that ozone molecules appearing at 50 and 52 amu are produced predominantly from  $\text{Q} + \text{O}_2$  and  $\text{O} + \text{Q}_2$  collisions, respectively. The difference spectrum, normalized to the signal for  $\text{O}_3$  at 48 amu, is presented in Fig. 2(a).

To understand this spectrum recall that to first order  $[\text{Q}_2] = [\text{O}_2]$  and  $[\text{Q}] = [\text{O}]$  (taking  $k_{\text{Q}} = k_{\text{O}}$  for the moment). If reactions (1) had identical rate coefficients, Eqs. (3) imply that all four peaks in Fig. 2(a) should be the same size. With the dramatic exception of 52 amu this is more or less what one observes. A more refined expectation recognizes the actual composition of the mixture and, more importantly, that  $[\text{Q}] < [\text{O}]$  since  $k_{\text{Q}} > k_{\text{O}}$ . This is indicated in Fig. 2(a) as the “equal  $k$  prediction.” Again, except for the departure at 52 amu there is good agreement with the data. One can already draw one of the primary qualitative conclusions of this paper, namely that  $k_{\text{O}+\text{Q}_2} > k_{\text{O}+\text{O}_2} \approx k_{\text{Q}+\text{O}_2} \approx k_{\text{Q}+\text{Q}_2}$ , with  $k_{\text{O}+\text{Q}_2}$  exceeding the others by about 50%.

We repeated this simple experiment with an identical, but prescrambled, gas mixture; the resulting spectrum is indicated in Fig. 2(b). To understand this second spectrum recall that to first order one has  $[\text{OQ}] = 2[\text{Q}_2] = 2[\text{O}_2]$  and  $[\text{Q}] = [\text{O}]$  (again taking  $k_{\text{Q}} = k_{\text{O}}$ ), and that ozone molecules of

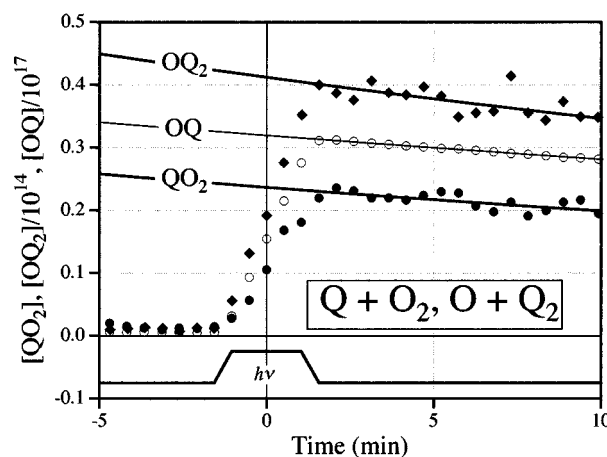


FIG. 3. Evolution of OQ (open circles),  $\text{OQ}_2$  (diamonds), and  $\text{QO}_2$  (filled circles) concentrations in the reaction cell during a typical measurement of  $k_{\text{O}+\text{Q}_2}$  and  $k_{\text{Q}+\text{O}_2}$ . The “ $h\nu$ ” curve indicates the duration of the photolysis period. Note the drastically different scales for OQ and the ozone species, as well as the clearly higher production rate of  $\text{OQ}_2$  compared with  $\text{QO}_2$ . Smooth curves are exponential fits to the data after photolysis.

mass 50 and 52 now arise from  $\text{O} + \text{OQ}$  and  $\text{Q} + \text{OQ}$  collisions as well. If all six rate coefficients were the same, one would expect the peaks at 48:50:52:54 amu to have relative sizes of 1:3:3:1. With the exception of the only slightly higher values at 50 and 52 amu (the familiar isotopic anomaly) this is what occurs. Our data agree fairly well with previously reported values of enrichments at these molecular masses including the slight depletion at 54 amu.<sup>5</sup>

In the quantitative experiments the unscrambled  $\text{N}_2:\text{O}_2:\text{Q}_2 \approx 80:10:10$  mixture was sealed off in the cell and the mass spectrometer monitored signals at mass positions corresponding to ozone and oxygen species continuously before, during, and after photolysis. Photolysis times were typically 2–3 min. Data before and after photolysis were fitted to exponentials and extrapolation of the fits to the midpoint of the photolysis period was used to determine concentration intervals,  $d[\text{X}]$ , as precisely as possible. A typical set of data for a run in which the  $\text{Q} + \text{O}_2$  and  $\text{O} + \text{Q}_2$  reactions were studied is shown in Fig. 3.

Interpretation of the concentration changes was carried out with the aid of Eqs. (3) and (4) together with the assumption that the partitioning of atoms between O and Q was in steady state. The experimental value of  $k_{\text{Q}}$ ,<sup>18</sup> the inequality  $k_{\text{Q}} > k_{\text{O}}$ , and the small effects of back-exchange arising from the production of OQ, were all included. The following expressions for three-body rate coefficients can be obtained with some effort (see Appendix B):

$$k_{\text{O}+\text{O}_2}[\text{M}] = 2k_{\text{O}}(d[\text{O}_3]/d[\text{OQ}])([\text{Q}_2]/[\text{O}_2])\beta_{\text{O}}, \quad (5a)$$

$$k_{\text{Q}+\text{O}_2}[\text{M}] = 2k_{\text{Q}}d[\text{QO}_2]/d[\text{OQ}]\beta_{\text{Q}}, \quad (5b)$$

$$k_{\text{O}+\text{Q}_2}[\text{M}] = 2k_{\text{O}}d[\text{OQ}_2]/d[\text{OQ}]\beta_{\text{O}}, \quad (5c)$$

$$k_{\text{Q}+\text{Q}_2}[\text{M}] = 2k_{\text{Q}}(d[\text{Q}_3]/d[\text{OQ}])([\text{O}_2]/[\text{Q}_2])\beta_{\text{Q}}. \quad (5d)$$

The  $\beta$  factors, which are close to unity in these experiments, account for the effects of back-exchange. At least eight runs were carried out at a total cell pressure near 200 Torr for each reaction. The results for  $k_Q/k_O=1.156$  are:  $k_{O+O_2}=(6.52\pm0.15)$ ,  $k_{Q+O_2}=(6.26\pm0.07)$ ,  $k_{O+Q_2}=(9.67\pm0.12)$ , and  $k_{Q+Q_2}=(6.25\pm0.07)\times10^{-34}$  cm<sup>6</sup>/s, where the indicated uncertainties refer to the mean value ( $1\sigma_m$ ) and reflect only the scatter in the measurements. For  $k_Q/k_O=1.245$ , one obtains  $k_{O+O_2}=(6.05\pm0.15)$  and  $k_{O+Q_2}=(8.98\pm0.12)$ , while  $k_{Q+O_2}$  and  $k_{Q+Q_2}$  remain unchanged. In either case, the qualitative observations discussed above are confirmed, indicating that  $k_{O+Q_2}$  is  $\approx 50\%$  larger than the average of the other three. It should be noted that these three-body rate coefficients were derived from measurements at a single pressure and with  $[Q_2]\approx[O_2]$ . Broader exploration of the parameter space is clearly called for, but is beyond the scope of this work.

## V. DISCUSSION

Three comparisons with the results of previous investigations will be made. First, we compare our  $k_{O+O_2}$  to that currently recommended for use in atmospheric modeling. Second, we discuss the connections between our rate coefficients and data on isotopic enrichments observed when ozone is produced in scrambled mixtures. This enables us to estimate rate coefficients for the ozone-forming reactions involving OQ that we have not measured directly here, and to test the theoretical predictions for  $k_Q/k_O$  presented in Appendix A. Finally, we make use of these estimates in comparing our results to those from the pulsed radiolysis experiments,<sup>3</sup> as well as the recent theoretical treatment given by Gellene.<sup>10</sup>

The value of  $(6.5\pm1.1)\times10^{-34}$  cm<sup>6</sup>/s for  $k_{O+O_2}$  is in good agreement with that currently recommended for atmospheric modeling,<sup>17</sup>  $(6.2\pm0.5)10^{-34}$  cm<sup>6</sup>/s, at 296 K. The uncertainty quoted here is dominated by that in  $k_Q$ ,  $(2.9\pm0.5)\times10^{-12}$  cm<sup>3</sup>/s,<sup>18</sup> which is nearly 17%. This uncertainty cancels out when comparing our rate coefficients with one another or ratios of our rate coefficients with similar ratios from other studies, but it must be included when making comparisons between any of our individual rate coefficients and those determined from other experiments.

Quantitative comparison of our rate coefficients with measurements of isotopic enrichments (i.e., abundances) arising from recombination in scrambled mixtures must include two additional ozone formation reactions:



as well as backward exchange (-2a) and (-2b), due to the large (equilibrium) concentrations of OQ present in such experiments. In this case it can be shown that enrichments for ozone produced in reactions (1a)–(1f) are related to the rate coefficients by:

$$e_{50}=(\alpha/3)(k_{Q+O_2}/k_{O+O_2})+(2/3)(k_{O+OQ}/k_{O+O_2})-1, \quad (6a)$$

$$e_{52}=(1/3)(k_{O+Q_2}/k_{O+O_2})+(2\alpha/3)(k_{Q+OQ}/k_{O+O_2})-1, \quad (6b)$$

$$e_{54}=(\alpha)(k_{Q+Q_2}/k_{O+O_2})-1, \quad (6c)$$

where  $e_m$  denotes the enrichment for ozone molecules of mass number  $m$ , and  $\alpha=([Q]/[O])/([Q]/[O])_{\text{stat}}$ , a parameter describing the deviation of the  $[Q]/[O]$  ratio from its statistical value due to the isotope exchange reactions. In scrambled mixtures,  $\alpha=0.924$  (Appendix C).

For  $M=O_2$ , under conditions otherwise similar to those employed here, Mauersberger *et al.*<sup>5</sup> have determined that  $e_{50}=0.130\pm0.010$ ,  $e_{52}=0.144\pm0.010$ , and  $e_{54}=-0.046\pm0.010$ . Inserting the  $k_{Q+Q_2}$  and  $k_{O+O_2}$  found with  $k_Q/k_O=1.156$  into Eq. (6c) yields  $e_{54}=-0.114\pm0.024$ , well below Mauersberger *et al.*'s result. The difference may indicate that the actual  $k_Q/k_O$  ratio differs from that calculated in Appendix A. A  $k_Q/k_O$  ratio of 1.245 reproduces Mauersberger *et al.*'s  $e_{54}$ . This choice has little impact on the principal findings of this paper, but for completeness we present numerical results for both cases in what follows.

For  $e_{50}$  and  $e_{52}$ , we solve Eqs. (6a) and (6b) for the unknown rate coefficients  $k_{O+OQ}$  and  $k_{Q+OQ}$ :

$$k_{O+OQ}/k_{O+O_2}=3\{(e_{50}+1)-(\alpha/3)(k_{Q+O_2}/k_{O+O_2})\}/2, \quad (7a)$$

$$k_{Q+OQ}/k_{O+O_2}=3\{(e_{52}+1)-(1/3)(k_{O+Q_2}/k_{O+O_2})\}/2\alpha, \quad (7b)$$

from which we obtain  $k_{O+OQ}/k_{O+O_2}=1.251\pm0.019$  and  $k_{Q+OQ}/k_{O+O_2}=1.055\pm0.027$ , with  $k_Q/k_O=1.156$ . For  $k_Q/k_O=1.245$ ,  $k_{O+OQ}/k_{O+O_2}$  decreases to  $1.217\pm0.019$  while  $k_{Q+OQ}/k_{O+O_2}$  is unchanged. The large difference between  $k_{O+OQ}$  and  $k_{Q+OQ}$  is a direct consequence of the fact that the  $Q+O_2$  reaction contributes almost nothing to  $e_{50}$ , while  $e_{52}$  arises predominantly from  $O+Q_2$ . Note that in the free atmosphere, as well as in laboratory experiments in scrambled mixtures,  $e_{50}$  arises mainly from reaction (1e) and not (1b).

The comparison of our results with the rate coefficient ratios reported by Sehested *et al.* for  $M=CO_2$  at 1 bar total pressure<sup>3</sup> is summarized in Table I. The agreement is poor, suggesting either some unrecognized flaw in one or both experiments or that the nature of  $M$  produces isotopic selectivity. Until now, discussion of isotopic anomalies in ozone has focused on the complex formation step of  $O+O_2$  recombination. If the strong variation of the isotopomer-specific rate coefficients with  $M$  suggested in Table I holds up to further scrutiny, this discussion must be broadened to include the energy transfer steps.

To illustrate this, consider the  $O+Q_2$  and  $Q+O_2$  reactions in the context of a simple Lindemann model incorporating only complex association/dissociation and energy transfer processes:

TABLE I. Recombination rate coefficient ratios for selected isotopic variants of O+O<sub>2</sub>+M, as % deviation from unity.

Rate coefficients	Sehested, <i>et al.</i> <sup>a</sup> (M=CO <sub>2</sub> , <i>p</i> = 1 bar)	This work (M=80% N <sub>2</sub> , 20% O <sub>2</sub> )	
		<i>k<sub>Q</sub></i> / <i>k<sub>O</sub></i> = 1.156	<i>k<sub>Q</sub></i> / <i>k<sub>O</sub></i> = 1.245
( <i>k<sub>O+Q<sub>2</sub></sub></i> + <i>k<sub>Q+O<sub>2</sub></sub></i> )/2 <i>k<sub>O+O<sub>2</sub></sub></i>	14.7±2.8	22.2±2.4	25.9±2.4
( <i>k<sub>O+OQ</sub></i> + <i>k<sub>Q+OQ</sub></i> )/2 <i>k<sub>O+O<sub>2</sub></sub></i>	3.6±2.4	15.3±1.7	13.6±1.7
<i>k<sub>Q+Q<sub>2</sub></sub></i> / <i>k<sub>O+O<sub>2</sub></sub></i>	9.8±2.6	−4.1±2.6	+3.3±2.6

<sup>a</sup>Reference 3.

The rate coefficient for isotope exchange is  $k_a k_{-ax}/k_d$  (where  $k_d = k_{-a} + k_{-ax}$ ), while the low-pressure limiting rate coefficient for the overall recombination process,  $k_o$ , is given by  $k_{et} k_a/k_d$ . Other things being equal, faster association should be reflected in both exchange and recombination.

Instead, however, O+Q<sub>2</sub> is ≈20% slower than Q+O<sub>2</sub> in exchange, but ≈50% faster in recombination. To recoup this association disadvantage, the OQ<sub>2</sub><sup>‡</sup> complex must have more efficient energy transfer characteristics and/or a longer lifetime than does QO<sub>2</sub><sup>‡</sup>. Neither is readily understandable in terms of a single reaction channel. The participation of two channels with rather different complex lifetimes, however, could account for this behavior, since the short-lived channel would dominate exchange and the long-lived one would dominate recombination at low pressures. Such bimodal distributions in complex lifetimes may come about subtly as a result of dynamics, as indicated in trajectory studies of O+O<sub>2</sub> isotope exchange,<sup>19,20</sup> or more explicitly due to the involvement of more than one electronic state.

In closing this section we relate our observations to the recent theoretical model of symmetry-induced kinetic isotope effects (SIKIEs) developed by Gellene.<sup>10</sup> The principal feature of this model is that when the diatomic involved in the O+O<sub>2</sub> collision is homonuclear (e.g., O<sub>2</sub>, Q<sub>2</sub>), only a fraction of the rotational states (*f*-parity) correlate with those of the ozone molecule that would result from recombination. When the diatomic is heteronuclear (e.g., OQ), all of its rotational states (both *e*- and *f*-parities) correlate with those of the resulting ozone molecule. Isotopic enrichments occur via depression of the rate coefficient for O+O<sub>2</sub> recombination relative to those for processes involving isotopically heteronuclear diatomics, such as O+OQ. Gellene has shown that the pattern of isotopic enrichments reported by Mauersberger *et al.*<sup>1,5</sup> can be accounted for in this way.<sup>10</sup>

Unfortunately, the present results are inconsistent with Gellene's model in two respects. First, the depression predicted for O+O<sub>2</sub> also applies to Q+O<sub>2</sub>, O+Q<sub>2</sub> and Q+Q<sub>2</sub>, such that these four recombination rate coefficients should be similar. This is clearly at odds with the large departure of

$k_{\text{O}+\text{Q}_2}$  from the other three that we observe here. Second, the rate coefficients for O+OQ and Q+OQ recombination should be very similar to one another and both should be larger than those for the processes involving the homonuclear diatomics. Again, our observation that  $k_{\text{Q}+\text{OQ}} \approx k_{\text{Q}+\text{Q}_2}$  while  $k_{\text{O}+\text{OQ}} > k_{\text{Q}+\text{OQ}}$  stands in contrast to the model predictions.

## VI. CONCLUSIONS

We have conducted experiments to isolate the reactions (1a)–(1d) and to determine their rate coefficients for M = 80% N<sub>2</sub>:10% O<sub>2</sub>:10% Q<sub>2</sub> at 200 Torr near room temperature (296 K). Our  $k_{\text{O}+\text{O}_2}$  is in good agreement with the current recommended value for O+O<sub>2</sub> recombination.  $k_{\text{Q}+\text{O}_2}$  and  $k_{\text{Q}+\text{Q}_2}$  are approximately equal to  $k_{\text{O}+\text{O}_2}$ , while  $k_{\text{O}+\text{Q}_2}$  is about 50% larger. These results are only weakly dependent on the ratio of rate coefficients for O-atom exchange,  $k_{\text{Q}}/k_{\text{O}}$ . Analysis of the results from earlier studies of enrichments in scrambled mixtures suggests that  $k_{\text{Q}+\text{OQ}}$  is close to  $k_{\text{O}+\text{O}_2}$ , while  $k_{\text{O}+\text{OQ}}$  is about 20% larger.

These data contradict the commonly accepted asymmetry-advantage hypothesis that has pervaded discussion of the heavy ozone anomaly since the first report of their insensitivity to substituent mass,<sup>2</sup> and recently taken explicit form in Gellene's rotational state correlation rule model.<sup>10</sup> Comparison with the results from recent pulsed radiolysis studies using M=CO<sub>2</sub> suggests there is a real sensitivity of the recombination rate coefficients to the nature of M. Clearly, the processes which produce these anomalous isotope effects are both more subtle and more dramatic than previously thought.

Several new avenues of research are suggested by these results. First, experiments of the type reported here should be repeated using <sup>17</sup>O in combination with O and Q. These would explore the full range of mass combinations and it would be fascinating to see whether the same pattern of rate coefficients that we have observed here occurs in these systems. Second, the M-sensitivity of these rate coefficients deserves further study. The series of noble gases, He, Ne, Ar, Kr, and Xe would reveal a good deal about the energy transfer dynamics without the complications of possible vibrational resonance effects, while in the other extreme one can imagine using isotopic substitution in the quencher (i.e., CQ<sub>2</sub>) to probe resonance effects in some detail. Third, the variation of these rate coefficients with pressure and tem-

perature should be investigated. This has been done in selected scrambled mixtures, but these represent mainly the O+OQ reactions and their <sup>17</sup>O counterparts. The present results indicate it may be unwise to assume this behavior applies to the other reactions. The obvious first candidate for such a study is O+Q<sub>2</sub>. Fourth, the relative rates of the Q+O<sub>2</sub> and O+Q<sub>2</sub> exchange reactions should be reexamined experimentally and theoretically. The comparison between our rate coefficients and the existing enrichment data for Q<sub>3</sub> suggests that simple rate theory underpredicts the  $k_Q/k_O$  ratio by  $\approx 8\%$ . Previous experimental studies of the exchange reactions have focused on determining the overall value of either  $k_Q$  or  $k_O$  and have assumed the two are equal in order to simplify analysis of the data. Finally, it is clear that a consistent theoretical picture of the ozone isotope anomalies is still not in hand. It would be useful to explore whether the rotational state correlation model of Gellene can be modified to account for the individual rate coefficients we have observed, perhaps by combining it with a dual-channel recombination mechanism. Possible origins for such a dual-channel mechanism, as well as for enhancements in energy transfer and/or complex lifetime, should also be investigated.

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## APPENDIX A: THE $k_Q/k_O$ RATIO

The  $k_Q/k_O$  ratio plays a central role in understanding the connection between studies of kinetics and measurements of isotopic abundances. Calculation of this ratio is nontrivial because reactions (2a) and (2b) are not a forward/reverse pair for which a simple equilibrium constant would suffice. We therefore adapt fundamental reaction rate theory as outlined by Johnston<sup>21</sup> to the present atom–diatom cases to find:

$$k_Q/k_O = \frac{(f_{t_3}f_{r_3}f_{v_1}f_{v_2})_{QO_2}(f_{t_2}f_{r_2}f_{v_1})_{Q_2}(f_t)_O}{(f_{t_3}f_{r_3}f_{v_1}f_{v_2})_{OQ_2}(f_{t_2}f_{r_2}f_{v_1})_{O_2}(f_t)_Q}, \quad (A1)$$

or more simply,

$$k_Q/k_O = C_{t_3}C_{t_2}C_{t_1}C_{r_3}C_{r_2}C_{v_1}C_{v_2}C_v, \quad (A2)$$

where the  $C_i$  denote ratios of the relevant partition functions,  $f_i$ . The subscripts  $t$ ,  $r$ , and  $v$  (as well as  $v_1$  and  $v_2$ ) refer to the translational, rotational, and vibrational degrees of freedom, respectively, while 3, 2, and 1 denote the triatomic complexes at their transition states, the diatoms, and the atoms. Note that (A1) reduces to the expected equilibrium constant when applied to a forward–reverse reaction pair [such as (2a) and (–2a)] because the triatomic partition functions are identical.

The ratios for translation and rotation are easily found from the partition functions given by Johnston.<sup>21</sup>

$$C_{t_3} = (f_t)_{QO_2}/(f_t)_{OQ_2} = (m_{QO_2}/m_{OQ_2})^{3/2} = (50/52)^{3/2}, \quad (A3a)$$

$$C_{t_2} = (f_t)_{Q_2}/(f_t)_{O_2} = (m_{Q_2}/m_{O_2})^{3/2} = (36/32)^{3/2}, \quad (A3b)$$

$$C_{t_1} = (f_t)_O/(f_t)_Q = (m_O/m_Q)^{3/2} = (16/18)^{3/2}, \quad (A3c)$$

$$C_{r_3} = \{(I_x I_y I_z)_{QO_2}/(I_x I_y I_z)_{OQ_2}\}^{1/2}, \quad (A3d)$$

$$C_{r_2} = I_{Q_2}/I_{O_2} = m_Q/m_O = 18/16. \quad (A3e)$$

All are trivial except  $C_{r_3}$ , for which we assumed that the transition state geometries for the two reactions are the same as, or at least deviate in a complementary way from, the  $C_{2v}$  configuration of the ground state O<sub>3</sub> molecule. This yields  $C_{r_3} = 0.957$ , independent of bond length and nearly independent of bond angle, and one obtains:

$$C_{t_3}C_{t_2}C_{t_1}C_{r_3}C_{r_2} = 1.015. \quad (A4)$$

We evaluate the vibrational partition function ratios in the low-temperature limit. The triatomic factors become:

$$C_{v_1}C_{v_2} = e^{\{(\nu_{1OQ_2} - \nu_{1QO_2}) + (\nu_{2OQ_2} - \nu_{2QO_2})\}/2kT} = e^{36.86 \text{ cm}^{-1}/2kT}, \quad (A5)$$

where we use  $\nu_{2OQ_2} = 677.503 \text{ 82 cm}^{-1}$  (Ref. 22) and  $\nu_{2QO_2} = 684.6134 \text{ cm}^{-1}$  (Ref. 23) and estimated the difference  $\nu_{1OQ_2} - \nu_{1QO_2}$  to be the average of the  $\nu_1$  shifts for central atom O-substitution for O<sub>3</sub>→OQO and QOQ→Q<sub>3</sub> using the  $\nu_1$  frequencies given for O<sub>3</sub> (1103.137 28 cm<sup>–1</sup>) (Ref. 24), OQO (1074.307 56 cm<sup>–1</sup>) (Ref. 25), QOQ (1072.2172 cm<sup>–1</sup>) (Ref. 26) and Q<sub>3</sub> (1041.5556 cm<sup>–1</sup>) (Ref. 26). This yields  $\nu_1(OQ_2) - \nu_1(QQ_2) \approx \{(\nu_1(OQO) - \nu_1(O_3)) + (\nu_1(Q_3) - \nu_1(QOQ))\}/2 = 29.75 \text{ cm}^{-1}$ . The diatomic term is found from the vibrational frequency for O<sub>2</sub> (1580.361 cm<sup>–1</sup>) and the conventional harmonic oscillator prediction that  $\nu_{Q_2} = \nu_{O_2}\sqrt{16/18}$ , (Ref. 27) such that

$$C_v = e^{(\nu_{Q_2} - \nu_{O_2})/2kT} = e^{90.38 \text{ cm}^{-1}/2kT}, \quad (A6)$$

and the desired product of vibrational partition function ratios is

$$C_{v_1}C_{v_2}C_v = e^{+26.76 \text{ cm}^{-1}/kT}. \quad (A7)$$

Combining these terms yields the desired rate coefficient ratio,

$$k_Q/k_O = 1.015e^{+38.50/T}, \quad (A8)$$

which is 1.156 at 296 K, the temperature at which the current experiments were carried out.

As indicated in Secs. IV and V, our comparison of the present observations with previous measurements of Q<sub>3</sub> isotopic abundances in scrambled mixtures indicates that the experimental ratio may be significantly higher (1.245). In the present context this can only arise from differences in transition state geometries or lower vibrational frequencies. The former could lead to a larger  $C_{r_3}$  ratio, but the required difference in transition state geometries is large. The energy

differences involved [i.e., (2a) is  $\approx 22.6 \text{ cm}^{-1}$  exothermic while (2b) is endothermic by a similar amount] are small compared to those produced by the changes in molecular geometry needed to account for the change in  $C_{r3}$ . The changes in vibrational frequencies needed to account for the experimental result also seem extreme—both  $\nu_1$  and  $\nu_2$  would need to decrease by about a factor of two. Further investigation of this point is clearly warranted, but is beyond the scope of this paper.

## APPENDIX B: EXPRESSIONS FOR THREE-BODY RATE COEFFICIENTS

The  $[\text{OQ}]=0$  limit of relations (5a)–(5d) can be obtained quickly from Eqs. (3a)–(3d) with the assumption that photolysis and recombination are in steady state. The exchange reactions (2a) and (2b) are much faster than recombination, so the partitioning of atoms between O and Q is also in steady state:

$$d[\text{O}]/dt = -k_{\text{O}}[\text{O}][\text{Q}_2] + k_{\text{Q}}[\text{Q}][\text{O}_2] = 0, \quad (\text{B1})$$

from which

$$[\text{Q}]/[\text{O}] = (k_{\text{O}}/k_{\text{Q}})[\text{Q}_2]/[\text{O}_2]. \quad (\text{B2})$$

$[\text{Q}]$  can be found from this last relation and substituted into Eq. (4) to determine  $[\text{O}]$  in terms of  $d[\text{OQ}]/dt$ . Use of the resulting expression for  $[\text{O}]$  in Eq. (3a) immediately yields Eq. (5a) apart from the factor  $\beta_{\text{O}}$ , since the  $\beta_i=1$  when  $[\text{OQ}]=0$ . Similar manipulations produce the  $[\text{OQ}]=0$  limits of Eqs. (5b)–(5d).

As photolysis proceeds,  $[\text{OQ}]$  increases at the expense of  $[\text{Q}_2]$  and  $[\text{O}_2]$ , and the effects of back-exchange (-2a), (-2b) must be included in the expression for  $d[\text{O}]/dt$ . From this one finds:

$$[\text{Q}]/[\text{O}] = \frac{k_{\text{O}}[\text{Q}_2] + k_{\text{Q}}[\text{OQ}]}{k_{\text{Q}}[\text{O}_2] + k_{\text{O}}[\text{OQ}]}, \quad (\text{B3})$$

which reduces to (B2) when  $[\text{OQ}]=0$ . The algebra is more laborious, but it is straightforward to solve for  $[\text{Q}]$ , find  $[\text{O}]$  in terms of  $d[\text{OQ}]/dt$ , and insert this into Eq. (3a) to obtain Eq. (5a) and thereby the definition of  $\beta_{\text{O}}$ . Equations (5b)–(5d) follow from similar manipulations. The factors  $\beta_{\text{O}}$  and  $\beta_{\text{Q}}$  are represented compactly by  $\beta_{\text{O}}=u/u_{\text{O}}$  and  $\beta_{\text{Q}}=u/u_{\text{Q}}$ , where:

$$u = 1 - (k_{-\text{O}}/k_{\text{O}})(k_{-\text{Q}}/k_{\text{Q}})[\text{OQ}]^2/([\text{Q}_2][\text{O}_2]), \quad (\text{B4a})$$

$$u_{\text{O}} = 1 + (k_{-\text{O}}/k_{\text{Q}})[\text{OQ}]/[\text{O}_2], \quad (\text{B4b})$$

$$u_{\text{Q}} = 1 + (k_{-\text{Q}}/k_{\text{O}})[\text{OQ}]/[\text{Q}_2]. \quad (\text{B4c})$$

These reduce to unity (as do  $\beta_{\text{O}}$  and  $\beta_{\text{Q}}$ ) as  $[\text{OQ}]$  approaches zero such that Eqs. (3a)–(3d) are reproduced.

## APPENDIX C: THE $[\text{Q}]/[\text{O}]$ RATIO IN SCRAMBLED ISOTOPIC MIXTURES

The steady-state  $[\text{Q}]/[\text{O}]$  ratio in a mixture of oxygen molecules containing only O and Q atoms varies with the amount of OQ according to Eq. (B3). In unscrambled mix-

tures  $[\text{OQ}]=0$  and (B3) reduces to (B2). Moreover, since the statistically expected  $[\text{Q}]/[\text{O}]$  ratio is  $[\text{Q}_2]/[\text{O}_2]$  in this case,

$$[\text{Q}]/[\text{O}] = (k_{\text{O}}/k_{\text{Q}})[\text{Q}]/[\text{O}]_{\text{stat}}. \quad (\text{C1})$$

For  $k_{\text{Q}}/k_{\text{O}}=1.156$  (or 1.245) one obtains:

$$[\text{Q}]/[\text{O}] = 0.866 \text{ (or } 0.803) \times [\text{Q}]/[\text{O}]_{\text{stat}}. \quad (\text{C2})$$

In fully scrambled mixtures, on the other hand, the diatomic species concentrations reach equilibrium.  $[\text{Q}]/[\text{O}]$  is found by inserting the equilibrium molecular concentrations into Eq. (B3) and a different result is obtained.

With the aid of atom conservation, the set of five equations for  $[\text{O}_2]$ ,  $[\text{OQ}]$ ,  $[\text{Q}_2]$ ,  $[\text{O}]$ , and  $[\text{Q}]$  that result from the steady-state assumption can be solved in a straightforward fashion. We omit the lengthy derivation here because at room temperature the diatom concentration ratios are approximated very well by those one would expect based solely on permutation statistics. That is, if  $q$  denotes the fraction of the total number of atoms in the system that are Q-atoms, it is an excellent approximation to take  $[\text{O}_2]/[\text{O}_2]_{\text{T}} = (1-q)^2$ ,  $[\text{Q}_2]/[\text{O}_2]_{\text{T}} = q^2$ , and  $[\text{OQ}]/[\text{O}_2]_{\text{T}} = 2q(1-q)$ , where  $[\text{O}_2]_{\text{T}} = [\text{O}_2] + [\text{OQ}] + [\text{Q}_2]$ . Use of these results in Eq. (B3) yields

$$[\text{Q}]/[\text{O}] = [\text{Q}]/[\text{O}]_{\text{stat}} \frac{k_{\text{O}}q + 2k_{-\text{Q}}(1-q)}{k_{\text{Q}}(1-q) + 2k_{-\text{O}}q}, \quad (\text{C3})$$

in which  $[\text{Q}]/[\text{O}]_{\text{stat}}$  is the statistically expected atom concentration ratio  $q/(1-q)$ . This can be reduced to:

$$[\text{Q}]/[\text{O}] = [\text{Q}]/[\text{O}]_{\text{stat}} \frac{2k_{-\text{Q}}}{k_{\text{Q}}} \frac{1 + q\{k_{\text{O}}/2k_{-\text{Q}} - 1\}}{1 + q\{2k_{-\text{O}}/k_{\text{Q}} - 1\}}. \quad (\text{C4})$$

The factors in curly brackets are small because the reverse exchange reactions (-2a), (-2b) are approximately half as fast as their forward counterparts (2a), (2b). Expanding the denominator and retaining terms to first order in  $q$  yields

$$[\text{Q}]/[\text{O}] \approx [\text{Q}]/[\text{O}]_{\text{stat}} \times 2k_{-\text{Q}}/k_{\text{Q}}(1 + qU), \quad (\text{C5})$$

where  $U = (k_{\text{O}}/k_{\text{Q}})\{k_{\text{Q}}/2k_{-\text{Q}} - 2k_{-\text{O}}/k_{\text{O}}\}$  is very small; insertion of the equilibrium constants yields  $\{ \} \approx 2.8 \times 10^{-4}$ . One can therefore write:

$$[\text{Q}]/[\text{O}] \approx [\text{Q}]/[\text{O}]_{\text{stat}} \times 2k_{-\text{Q}}/k_{\text{Q}}. \quad (\text{C6})$$

At first it is puzzling that the rate coefficients for reaction (2a), (-2a) appear in preference to those for (2b), (-2b), but further exploration shows that this is an artifact of choosing  $q$  as the variable describing the atomic abundances. If one instead selects  $s = (1-q)$ , one obtains an expression similar to (C5) that reduces to:

$$[\text{Q}]/[\text{O}] \approx [\text{Q}]/[\text{O}]_{\text{stat}} \times k_{\text{O}}/2k_{-\text{O}}. \quad (\text{C7})$$

Both (C6) and (C7) yield:

$$[\text{Q}]/[\text{O}] \approx [\text{Q}]/[\text{O}]_{\text{stat}} \times 0.924. \quad (\text{C8})$$

Note that this differs qualitatively from the  $[\text{OQ}]=0$  case, Eq. (C2). The partitioning of atoms evolves from that given



by Eq. (C2) to that given by Eq. (C6) or (C7) as the molecular composition evolves from unscrambled to its equilibrium state.

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