

# Lawrence Berkeley National Laboratory

## Recent Work

### Title

EVIDENCE FOR LONG-LIVED COLLISION COMPLEXES IN ION-MOLECULE REACTIONS:  $\text{DO}_2^+$  FROM  $\text{O}_2^+$  AND  $\text{D}_2$

### Permalink

<https://escholarship.org/uc/item/11j3n3b6>

### Authors

Gislason, E.A.  
Mahan, Bruce H.  
Tsao, Chi-wing  
et al.

### Publication Date

1969-04-01

Submitted to the Journal  
of Chemical Physics

RECEIVED  
LAWRENCE  
RADIATION LABORATORY

UCRL-18836  
Preprint

APR 23 1969

ey 2

LIBRARY AND  
DOCUMENTS SECTION

EVIDENCE FOR LONG-LIVED COLLISION COMPLEXES IN  
ION-MOLECULE REACTIONS:  $DO_2^+$  FROM  $O_2^+$  AND  $D_2$

E. A. Gislason, Bruce H. Mahan, Chi-wing Tsao, and  
Arthur S. Werner

April 1969

AEC Contract No. W-7405-eng-48

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy  
which may be borrowed for two weeks.  
For a personal retention copy, call  
Tech. Info. Division, Ext. 5545*

LAWRENCE RADIATION LABORATORY  
UNIVERSITY of CALIFORNIA BERKELEY

UCRL-18836

## **DISCLAIMER**

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Submitted to the Journal  
of Chem. Physics

UCRL-18836  
Preprint

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory  
Berkeley, California

AEC Contract No. W-7405-eng-48

EVIDENCE FOR LONG-LIVED COLLISION COMPLEXES IN

ION-MOLECULE REACTIONS:  $DO_2^+$  FROM  $O_2^+$  AND  $D_2$

E. A. Gislason, Bruce H. Mahan, Chi-wing Tsao, and  
Arthur S. Werner

April 1969

Evidence for Long-lived Collision Complexes in  
 Ion-Molecule Reactions:  $DO_2^+$  from  $O_2^+$  and  $D_2$ .

E. A. Gislason, Bruce H. Mahan, Chi-wing Tsao, and  
 Arthur S. Werner

Department of Chemistry, University of California, and  
 Inorganic Materials Research Division of the  
 Lawrence Radiation Laboratory, Berkeley, California.

Recently, there has been discussion concerning the importance of long-lived collision complexes in ion-molecule reactions.<sup>1</sup> Some collision complexes have lifetimes long enough ( $>10^{-6}$  sec) to permit direct detection by mass spectrometry.<sup>2</sup> Such detection is impossible for those complexes which survive only a few rotational periods ( $<10^{-10}$  sec). Measurement of the velocity vector distribution of the reaction products provides the least equivocal means of demonstrating the occurrence of these shorter-lived complexes. Such investigations<sup>3-7</sup> of the reactions  $N_2^+ (D_2, D) N_2D^+$ ,  $Ar^+ (D_2, D) ArD^+$ ,  $N_2^+ (CH_4, CH_3) N_2H^+$  and other<sup>8</sup> exothermic hydrogen atom transfers have shown that products are distributed asymmetrically in the center-of-mass coordinate system. Consequently, these reactions proceed, in the energy range investigated, by direct or very short-lived interaction mechanisms in which collision partners remain close for less than one rotational period. We report here measurements of the velocity distribution of  $DO_2^+$  from the endothermic ( $\Delta E_0^0 = 1.9$  eV) reaction  $O_2^+ (D_2, D) DO_2^+$

which strongly suggest that this process occurs via a collision complex which lasts several rotational periods.

Experiments were performed with the apparatus described earlier.<sup>6</sup> A microwave discharge in  $O_2$  produced  $O_2^+$ , and the method of Turner et al<sup>9</sup> showed that the momentum analysed beam contained less than 3%  $O_2^+$  in metastable excited electronic states. Reaction threshold measurements indicated that the average vibrational excitation of  $O_2^+$  was approximately 0.5 eV.

Figure 1a shows a typical contour map of the intensity of  $DO_2^+$  per unit velocity space volume. The distribution is very nearly isotropic, and the greatest intensity occurs at the center-of-mass velocity. While the symmetry of the intensity about the barycentric angles of  $\pm 90^\circ$  indicates the occurrence of a collision complex which lasts several rotational periods, the isotropy suggests that the angular momentum of the complex is relatively small, and its temperature, or internal energy per mode, is large.<sup>10</sup> This deduction is consistent with the relatively small total reaction cross section ( $< 1 \text{ \AA}^2$ ) and with the relatively large binding energy (2.6 eV) of  $D_2O_2^+$  with respect to  $O_2^+$  and  $D_2$ . The high intensity of product near the center-of-mass velocity indicates substantial internal excitation of the  $DO_2^+$ , which is to be expected if energy is distributed statistically among internal and translational modes of a decaying complex.

Figure 1b shows profiles along the 0-180° line of the intensity distributions of  $HO_2^+$  and  $DO_2^+$  from collisions of  $O_2^+$  with HD. The slight asymmetry about the center of mass velocity can be traced to interference of the  $O_2^+$  beam with the detection

of the forward scattered products. The isotope effect, which favors  $\text{DO}_2^+$  by a factor of eight, is opposite in sense to that found for products scattered in the ion beam direction from the reactions of  $\text{N}_2^+$  with HD and isotopic methanes,<sup>6,7</sup> but is the one to be expected if the collision complex were decaying according to statistical or phase space considerations.<sup>11</sup> The greater density of vibrational levels of  $\text{DO}_2^+$  and its lower zero point energy favor its formation.

Figure 1c shows profiles of the distribution of  $\text{DO}_2^+$  formed from  $\text{O}_2^+-\text{D}_2$  collisions of different relative energy. As the relative energy increases, the product distribution becomes asymmetric, and eventually displays the forward peaking characteristic of direct hydrogen atom abstractions. Transition from a long-lived complex to a direct interaction as the collision energy is increased is to be expected, since unimolecular reaction rate theory<sup>12</sup> shows that the lifetime with respect to dissociation of an excited molecule decreases and approaches  $10^{-14}$  sec as the excitation in excess of the dissociation threshold increases.

We believe that there are two significant reasons why the  $\text{O}_2^+ (\text{D}_2, \text{D}) \text{DO}_2^+$  reaction proceeds through a long-lived complex at lower energy. First, the  $\text{D}_2\text{O}_2^+$  intermediate represents a potential well whose depth, excluding activation barriers, is 2.6 eV with respect to reactants. Second, the reaction is endothermic by 1.9 eV. Consequently, the lifetime of the complex for a given initial energy is lengthened since the threshold

for dissociation to products is correspondingly high. Moreover, the direct reaction processes which might proceed with large cross section are excluded, since, for example, in order for an endothermic reaction to proceed via the ideal stripping process, the projectile energy relative to one atom must be greater than the endothermicity. Clearly, this condition is met only at projectile energies relative to the target molecule that exceed the minimum necessary for reaction.

A more detailed account of this reaction and of formation of the other ionic products  $\text{OH}^+$ ,  $\text{O}^+$ , and  $\text{H}_2\text{O}^+$  will be published later.

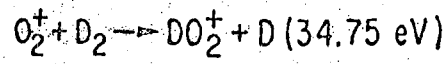
Acknowledgement: This work was supported by the U. S. Atomic Energy Commission.



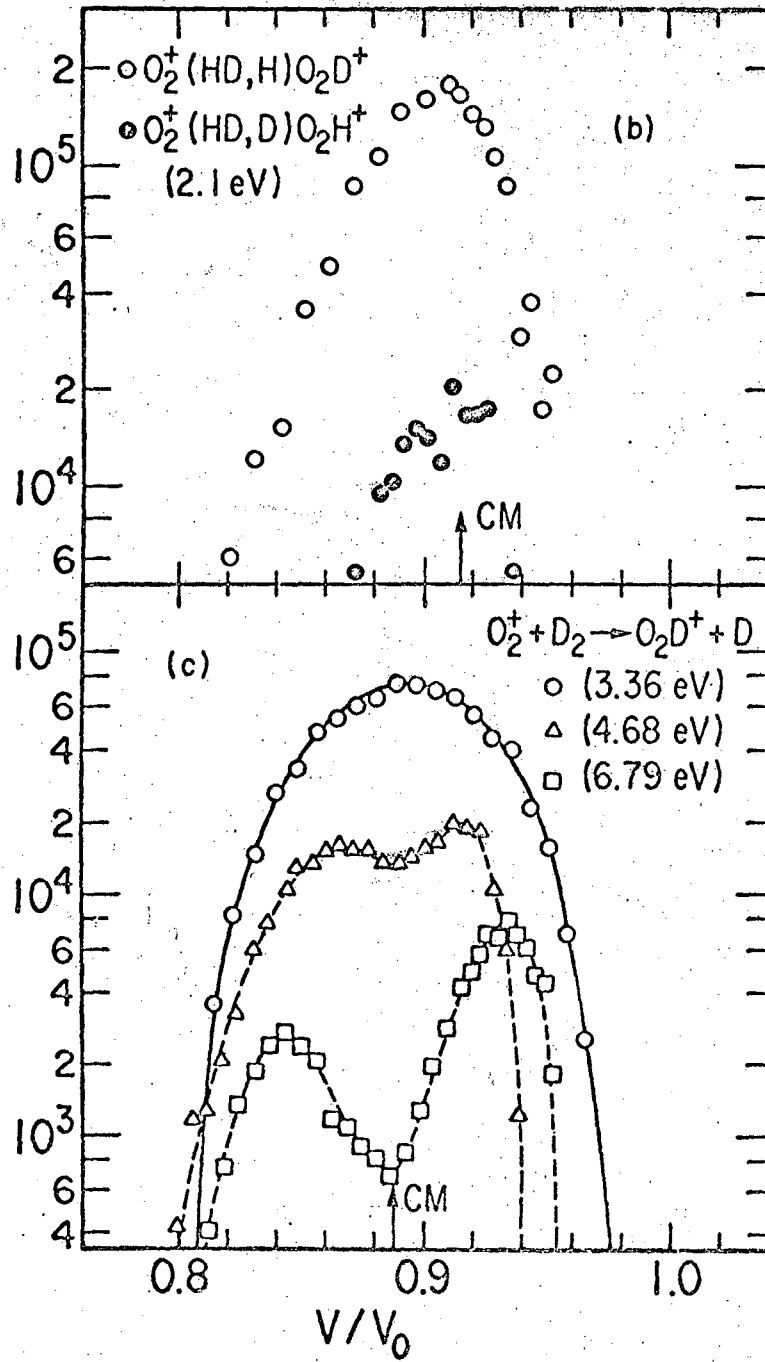
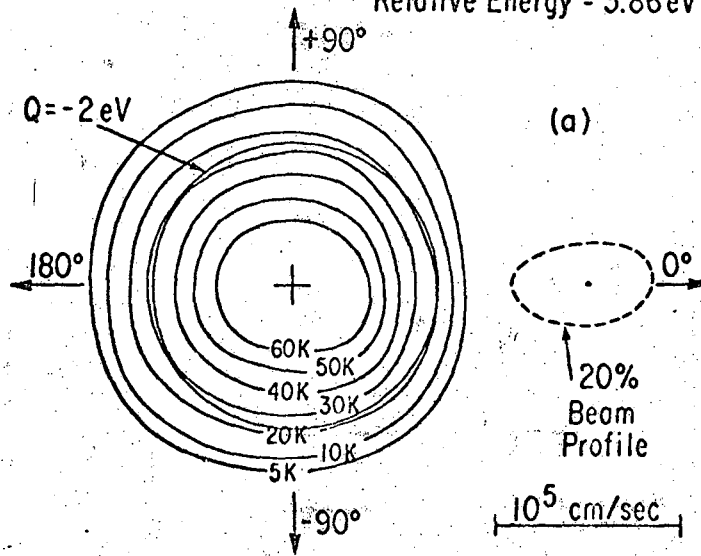
References

1. L. Friedman, *Ann. Rev. Phys. Chem.* 19, 273 (1968).
2. R. F. Pottie and W. H. Hamill, *J. Phys. Chem.* 63, 877 (1959).
3. L. D. Doverspike, R. L. Champion, and T. L. Bailey, *J. Chem. Phys.* 45, 4385 (1966).
4. Z. Herman, J. Kerstetter, T. Rose, and R. Wolfgang, *Disc. Faraday Soc.* 44, 123 (1967).
5. W. R. Gentry, E. A. Gislason, Y. T. Lee, B. H. Mahan, and C. W. Tsao, *Disc. Faraday Soc.* 44, 137 (1967).
6. W. R. Gentry, E. A. Gislason, B. H. Mahan, and C. W. Tsao, *J. Chem. Phys.* 49, 3058 (1968).
7. E. A. Gislason, B. H. Mahan, C. W. Tsao, and A. S. Werner, *J. Chem. Phys.* 50, 142 (1969).
8. Unpublished results, this laboratory.
9. B. R. Turner, J. A. Rutherford, and D. M. J. Compton, *J. Chem. Phys.* 48, 1602 (1968).
10. W. B. Miller, S. A. Safron, and D. R. Herschbach, *Disc. Faraday Soc.* 44, 108 (1967).
11. M. J. Pearson, B. S. Rabinovitch, and G. Whitten, *J. Chem. Phys.* 42, 2470 (1965).
12. D. L. Bunker, Theory of Elementary Gas Reaction Rates (Pergamon Press, Oxford, 1966).

Fig. 1 (a) A contour map in the center-of-mass system of the intensity per unit velocity space volume of  $\text{DO}_2^+$  from  $\text{O}_2^+-\text{D}_2$  collisions at 3.86 eV initial relative translational energy. The scattering from a stationary target gas with no beam energy and angle spread, and no initial internal excitation should fall within the circle marked  $Q = -2.0$ . (b) Intensities at  $0^\circ$  LAB of  $\text{DO}_2^+$  and  $\text{HO}_2^+$  from 2.1 eV collisions of  $\text{O}_2^+$  with HD, plotted as functions of  $v/v_0$ , the ratio of product to projectile laboratory velocity. (c) Intensities at  $0^\circ$  LAB <sup>cf</sup>  $\text{DO}_2^+$  from  $\text{O}_2^+-\text{D}_2$  collisions at three relative energies. The greater spread of the 3.36 eV experiment is due to the relatively greater importance of initial internal excitation of  $\text{O}_2^+$ .



Relative Energy = 3.86 eV



LEGAL NOTICE

*This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:*

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or*
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.*

*As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.*

1 2  
3 1 0 6

TECHNICAL INFORMATION DIVISION  
LAWRENCE RADIATION LABORATORY  
UNIVERSITY OF CALIFORNIA  
BERKELEY, CALIFORNIA 94720