GEOPHYSICAL RESEARCH LETTERS, VOL. 24, NO. 2, PAGES 119-122, JANUARY 15, 1997

Fine structure effects in the O^+– O collision frequency

A. P. Hickman, M. Medikeri-Naphade, and C. D. Chapin

Department of Physics, Lehigh University, Bethlehem, PA

D. L. Huestis

Molecular Physics Laboratory, SRI International, Menlo Park, CA

Abstract. Effects of the fine structure of atomic oxygen on the O^+– O ion-neutral momentum transfer collision frequency ν_{in} are investigated to assess whether they could account for persistent discrepancies between theoretical calculations and values of ν_{in} determined from observations. Potential curves for the molecule have been calculated that include spin-orbit effects and properly dissociate to the three asymptotic limits O^+–$O(^3P_J)$ (J=2,1,0). Coupled channel scattering calculations have been performed to determine ν_{in}. The results show that ν_{in} depends strongly on the initial fine structure level, and the average over a thermal distribution of initial states is a few percent smaller than recent theoretical calculations that neglect fine structure effects. The most recent analysis of observations leads to values of ν_{in} about 30% smaller than older values. The theoretical calculations are now consistent with the most recent experimental determinations of ν_{in}.

Introduction

Collisions between O^+ and O are very important in the upper atmosphere. The collision frequency ν_{in} plays a crucial role in models of global wind circulation and in determining the ion density in the ionosphere. Over a period of years, there has been a significant discrepancy between calculated values of ν_{in} and values inferred from aeronomic experiments.

The $O(^3P)$ ground state is split into three fine structure levels ^3P_J (J=2,1,0). The energies of these levels depend on how the electron spins are aligned, and the spin alignment also affects the collision dynamics. The inset in Fig. 1 shows the energy levels. The splitting between the J=2 and J=0 levels corresponds to kT for T=326 K. Since the range of important temperatures for aeronomic applications is approximately $T \sim 300 - 2000$ K, this splitting is clearly not negligible. However, previous calculations of ν_{in} have ignored the fine structure splitting of atomic oxygen as well as spin-orbit and rotational coupling between states of O_2^+ during the collision.

Paper number 96GL03797.
0094-8534/97/96GL-03797$05.00

Early calculations of ν_{in} were performed by *Dalgarno* [1958, 1964], *Knof et al.* [1964], *Banks* [1966], and *Stubbe* [1968]. Because of concern that these theoretical calculations were not consistent with the value of ν_{in} that best fit the aeronomic measurements, *Burnside et al.* [1987] proposed increasing the ν_{in} of *Banks* [1966] by a factor of 1.7. This factor was based on comparing neutral wind speeds obtained from incoherent scatter radar with those from Fabry-Perot measurements, which determine the Doppler shift of the $O(^1D)$ emission at 630 nm. *Salah* [1993] showed that other experiments could also be brought into mutual consistency by increasing the ν_{in} of *Banks* by the factor of 1.7. In comparison, the most recently published theoretical calculations [*Stallcop et al.*, 1991; *Pesnell et al.*, 1993] favor an increase of about 1.3 over *Banks'* values. A discrepancy of this size (~30%) causes concern because ν_{in} is crucial to so many atmospheric models.

The disagreement over the value of ν_{in} has led several groups to reexamine the issue. The present work addresses the collision theory. *Omidvar and Pesnell.* [1995] investigated the effect of the relative drift velocity of the ion and neutral winds and concluded that this effect was small (~1%). Other recent studies have considered the validity of the methodology used to analyze the observational data. *Reddy et al.* [1994], *Davis et al.* [1995], and *Buonsanto et al.* [1996] have investigated the details of how ν_{in} has been extracted from aeronomic observations. They investigated the effect of scatter and systematic error in the observational data. The most recent correction to *Banks'* results, obtained by *Buonsanto et al.*, is an increase by a factor of 1.2 ± 0.2.

Molecular Potential Curves

The calculations are based on molecular potential curves for O_2^+ that include spin orbit effects. We determined these curves by starting with the potentials of *Stallcop et al.* [1991] and then adding spin-orbit effects using the method of *Cohen and Schneider* [1974]. The Hamiltonian $H(R)$ at each internuclear separation R consists of an electronic component and a spin-orbit component :

$$H(R) = H_{el} + H_{so}. \quad (1)$$

The potential curves of *Stallcop et al.* [1991] provide matrix elements of H_{el} in a set of states corresponding to

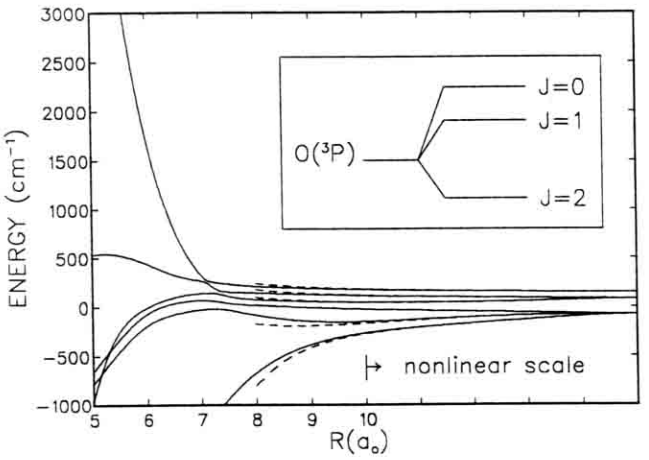

Figure 1. Selected adiabatic curves for O_2^+ including spin-orbit effects. Curves for $\Omega = 3/2$ are shown. The solid lines are gerade symmetry; the dashed lines show the ungerade curves in the regime where they begin to separate from the gerade curves. The inset shows the energy levels of atomic oxygen: $E_J = 0, 158.5$, and $226.5\,\mathrm{cm}^{-1}$ for $J = 2, 1, 0$, respectively.

particular values of the molecule's angular momentum quantum numbers in the LS coupling scheme. Following *Durup* [1981], we use the notation $|LS\Lambda\Omega\rangle$ to denote these states. L, the total orbital angular momentum quantum number, is 1 for the ground electronic state of $O(^3P)$. Λ gives the projection of L on the internuclear axis, and has the value 0 for Σ states and 1 for Π states. S gives the total spin. Each Σ or Π state may be a doublet ($S = 1/2$), a quartet ($S = 3/2$) or a sextet ($S = 5/2$). Ω is the projection of $L + S$ on the internuclear axis. All electronic states are also denoted either gerade or ungerade, but we will suppress this notation since the present section applies equally to either symmetry. The matrix elements of $H_{\mathrm{el}}(R)$ in the states $|LS\Lambda\Omega\rangle$ are given by

$$\langle LS'\Lambda'\Omega'|H_{\mathrm{el}}(R)|LS\Lambda\Omega\rangle = \delta_{S'S}\,\delta_{\Lambda'\Lambda}\,\delta_{\Omega\Omega'}\,V_{S\Lambda}(R). \quad (2)$$

The functions $V_{S\Lambda}(R)$ are the potential curves [*Stallcop et al.*, 1991] for the states $^{2S+1}\Lambda$ of O_2^+ ($\Lambda = \Sigma$ or Π).

We also need the matrix elements of H_{so}. In the asymptotic limit ($R \to \infty$), these matrix elements may be determined from spectroscopic data. We assume that H_{so} is independent of R. Our results provide justification, *a posteriori*, for this approximation. It turns out that ν_{in} is insensitive to the details of H_{so} in the region of small R where the approximation might break down.

The matrix elements of H_{so} are most easily determined in a set of states corresponding to a different angular momentum coupling scheme. This scheme is

$$\mathbf{L}_{\mathrm{O}} + \mathbf{S}_{\mathrm{O}} = \mathbf{J}, \qquad \mathbf{J} + \mathbf{S}_+ = \mathbf{K},$$

where $\mathbf{L}_{\mathrm{O}}$ and $\mathbf{S}_{\mathrm{O}}$ are the orbital and spin angular momenta of O, $\mathbf{J}$ is the total angular momentum of O, and $\mathbf{S}_+$ is the total angular momentum (spin) of O^+. Writing the corresponding states $|JK\Omega\rangle$, we have

$$\langle J'K'\Omega'|H_{\mathrm{so}}|JK\Omega\rangle = \delta_{J'J}\,\delta_{K'K}\,\delta_{\Omega'\Omega}\,E_J, \quad (3)$$

where E_J denotes the energy of the atomic oxygen ^3P_J level.

Eqs. (2) and (3) provide the eigenvalues and eigenvectors, separately, of the operators $H_{\mathrm{el}}(R)$ and H_{so}. In order to evaluate explicitly the matrix elements of $H(R)$, we must write the matrix elements of $H_{\mathrm{el}}(R)$ and H_{so} in a common basis set. For the scattering calculations, it is convenient to choose the $|JK\Omega\rangle$ basis. This basis is related to the $|LS\Lambda\Omega\rangle$ basis by the following unitary transformation:

$$\langle LS\Lambda\Omega'|JK\Omega\rangle = \delta_{\Omega'\Omega}\,(-1)^{S+S_{\mathrm{O}}+S_+ +K-\Omega} \quad (4)$$
$$\times\sqrt{(2K+1)(2S+1)(2J+1)}$$
$$\times\left\{\begin{array}{ccc} L & S & K \\ S_+ & J & S_{\mathrm{O}} \end{array}\right\}\left(\begin{array}{ccc} L & S & K \\ \Lambda & \Omega-\Lambda & -\Omega \end{array}\right).$$

By using Eq. (4) to express the $|JK\Omega\rangle$ states in terms of the $|LS\Lambda\Omega\rangle$ states, we can evaluate the matrix elements $\langle J'K'\Omega'|H_{\mathrm{el}}|JK\Omega\rangle$. We then have all the matrix elements of $H(R)$ in the $|JK\Omega\rangle$ basis. Figure 1 shows selected adiabatic potential curves calculated from the total Hamiltonian $H(R)$. These curves are obtained at each R by diagonalizing the matrix $\langle J'K'\Omega'|H(R)|JK\Omega\rangle$. ($H(R)$ is already diagonal in Ω.) For small R, each curve becomes approximately equal to one of the $V_{S\Lambda}(R)$, and as $R \to \infty$, each potential curves approaches one of the three fine structure levels of atomic O. In contrast, the original curves of *Stallcop et al.* are all degenerate asymptotically.

Scattering Calculations

We have performed scattering calculations using the potential curves and coupling terms described above. The details of the work will be presented elsewhere, but the method follows *Hickman et al.* [1993]. For the present application, we must solve four sets of 18 coupled equations (two sets of gerade symmetry and two of ungerade) for each value of the total angular momentum quantum number. From the solutions to these equations we determine the momentum transfer (or diffusion) cross section in terms of the differential cross section for specific $J \to J'$ transitions:

$$Q_{\mathrm{D}}^{J\to J'}(E) = 2\pi\int_0^\pi \frac{d\sigma^{J\to J'}}{d\theta}(E)(1-\cos\theta)\sin\theta\,d\theta. \quad (5)$$

This expression is evaluated using methods developed by *Hickman and Smith* [1978]. We then sum over final states to obtain

$$Q_{\mathrm{D}}^{J}(E) = \sum_{J'=2}^{0} Q_{\mathrm{D}}^{J\to J'}(E). \quad (6)$$

A standard collision integral is

$$\Omega^J_{1,1}(T) = \tfrac{1}{2}\int_0^\infty Q^J_{\rm D}(xkT)\, x^2 e^{-x}\, dx, \qquad (7)$$

where $x = E/kT$, and E is the kinetic energy. Then the collision frequency is [*Pesnell et al.*, 1993]

$$\nu^J_{\rm in}(T) = \tfrac{2}{3}\sqrt{8kT/\pi\mu}\, N({\rm O})\, \Omega^{\rm J}_{1,1}({\rm T}), \qquad (8)$$

where μ is the reduced mass, and $N(\mathrm{O})$ is the oxygen number density. Note that $\nu^J_{\rm in}(T)$ depends on the specific initial level of atomic O in the collision. We define an average $\nu_{\rm in}(T)$ by weighting each $\nu^J_{\rm in}(T)$ by the relative populations of the initial J levels. Then

$$\nu_{\rm in}(T) = \sum_{J=2}^{0} w_J(T)\nu^J_{\rm in}(T). \qquad (9)$$

Recent work by *Sharma et al.* [1994] has demonstrated that the various fine structure levels of O are populated according to a thermal distribution up to an altitude of about 600 km. The weights are then given by

$$w_J(T) = \frac{(2J+1)\exp(-E_J/kT)}{\sum^0_{J'=2}(2J'+1)\exp(-E_{J'}/kT)}. \qquad (10)$$

At each T, $\nu_{\rm in}(T)$ is the weighted average of the $\nu^J_{\rm in}(T)$, with weights equal to the relative populations of oxygen J level at that temperature.

Results and Discussion

Figure 2 shows the results. The three dashed curves are the $\nu^J_{\rm in}(T)$, corresponding to the three possible initial fine structure level of $\mathrm{O}(^3P_J)$. The strong dependence of $\nu^J_{\rm in}(T)$ on the initial level is one of the major results of the present study. The solid line is the thermally averaged $\nu_{\rm in}(T)$, which should be compared with values determined from aeronomic observations. The dotted line shows the calculations of *Banks* [1966], multiplied by a factor of 1.25. This factor was chosen to make the scaled curve of *Banks* agree with the present results at $T = 1000\,\mathrm{K}$. The points attributed to *Stallcop et al.* [1991] were determined from the collision integrals tabulated in their paper. These results of *Stallcop et al.* and of *Pesnell et al.* [1993] are both single channel calculations based on the LS potential curves of *Stallcop et al.*

The strong dependence on J can be explained qualitatively. The asymptotic form of the potential curves includes a charge-quadrupole term, which behaves as CR^{-3}. The value of C is $-3.22\,\mathrm{eV\,\AA^3}$ for Σ states of O_2^+ and $+1.61\,\mathrm{eV\,\AA^3}$ for Π states. This term makes the Σ states lower in energy than the Π states asymptotically. Therefore the adiabatic potentials arising from the lowest fine-structure level (J=2) correlate preferentially with Σ states. However, the g/u splitting for a pair of Σ states is larger than for Π states [*Stallcop et al.*, 1991]. One can see in Fig. 1 that the g/u splitting of the lowest two states is visibly larger that for any other states. Previous work has invariably shown that the single feature of the potentials that has the largest effect on $\nu_{\rm in}$ is the rate of splitting of each pair of g/u potential curves. Faster splittings lead to a larger $\nu_{\rm in}$. This same behavior persists in the coupled channel calculations. Thus the values of $\nu^J_{\rm in}$ are the largest for J=2 levels because the those levels tend to correlate with Σ potential curves, which have a larger g/u splitting than the Π curves.

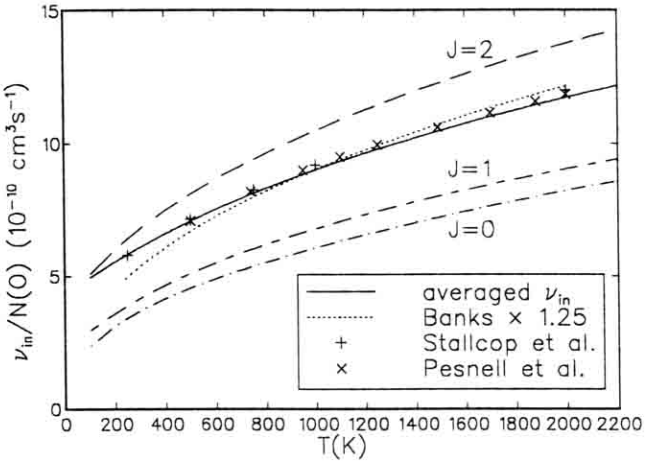

Figure 2. Calculated values of the collision frequency $\nu_{\rm in}$ as a function of temperature. The curves labelled $J = 2, 1, 0$ correspond to $\nu^J_{\rm in}(T)$ as defined in the text.

Figure 2 shows that when $\nu^J_{\rm in}(T)$ is averaged over the expected distribution of fine structure levels in the upper atmosphere, the results are slightly smaller than the previous calculations that neglected fine structure. The difference is small, so our results tend to confirm earlier calculations. However, note that there is in Fig. 2 a hint of problems with the single channel calculations based on the LS potential curves. These calculations correspond to fully mixed internal states of O. For $T > 500\,\mathrm{K}$, the populations of the J states are within about 20% of the fully mixed ($T \to \infty$) limit, and it is not surprising that the weighted average of the $\nu^J_{\rm in}(T)$ is very close to the single channel calculations. For $T < 200\,\mathrm{K}$, the lowest level, J=2, has an increasingly larger fraction of the total population, and the thermally averaged $\nu_{\rm in}$ approaches the result for J=2. In this case it is surprising that the single channel results, which correspond to full mixing, are so close to the coupled channel results for pure J=2. Careful examination of the underlying $Q^J_{\rm D}(E)$ has shown that the single channel method overestimates the cross sections at low energies where the CR^{-3} terms dominate the interaction.

The discrepancy between theoretical calculations of $\nu_{\rm in}$ and the results inferred from aeronomic measurements has been expressed as a "Burnside factor" F, which is the ratio between a particular value of $\nu_{\rm in}$ and the value calculated by *Banks* [1966]. Recent single channel theoretical calculations [*Stallcop et al.*, 1991;

Pesnell et al., 1993] have obtained $F \sim 1.3$. The present coupled channel results could be characterized by $F = 1.25$, but this factor applies only at $T = 1000\,\mathrm{K}$. (As shown in Fig. 2, all the recent theoretical results exhibit a somewhat weaker temperature dependence than *Banks'* results.) Three years ago, workers in the NSF-sponsored CEDAR program adopted the value $F = 1.7$ proposed by *Salah* [1993]. More recent work involving more sophisticated analysis of observational data has led to $F = 1.2 \pm 0.2$ [*Buonsanto et al.*, 1996]. The present theoretical results are fully consistent with this work.

The thermally averaged results for ν_{in} shown in Fig. 2 are fit by the following function:

$$\frac{\nu_{\mathrm{in}}(T)}{N(\mathrm{O})} = 5.92 \times 10^{-11}\, T^{-0.393}\, \left[1 + (96.6/T)^2\right]\ \mathrm{cm^3\,s^{-1}}.$$

This fit is within 1% for $300 \leq T \leq 4000\,\mathrm{K}$.

Recent work on the calculation of ν_{in} and its determination from aeronomic data has apparently resolved a long standing discrepancy . The present results, based on a coupled channel theory, confirm earlier calculations, at least in the range of energies important for aeronomic applications. At this point, the calculated values of ν_{in} are fully consistent with those derived by *Buonsanto et al.* [1996] from observations. The present study also has important implications for laboratory measurements of ν_{in}. Our results indicate that measured values of ν_{in} (or measured rates for the closely related process of charge exchange) will depend strongly on the distribution of initial fine structure levels. Comparison of laboratory results with atmospheric measurements should include an assessment of the laboratory distribution of initial oxygen fine structure levels.

Acknowledgments. This work was supported by NSF grant ATM-9409362. CDC was supported by the NASA Delaware Space Grant Consortium and by the REU program in the Physics Department at Lehigh University.

References

Banks, P., Collision frequencies and energy transfer: ions, *Planet. Space Sci., 14,* 1105–1122, 1966.

Buonsanto, M. J., Sipler, D. P., and Davenport, G. B., Estimation of the O^+, O Collision Cross Section from Coincident Radar and Fabry Perot Observations at Millstone Hill (abstract), *Eos Trans. AGU, 77*(17), Spring Meet. Suppl., S193, 1996.

Burnside, R. G., Tepley, C. A., and Wickwar, V. B., The O^+– O collision cross section: can it be inferred from aeronomical measurements? *Ann. Geophys., 5A,* 343–350, 1987.

Cohen, J. S. and Schneider, B. I., Ground and excited states of Ne_2 and Ne_2^+ I. Potential curves with and without spin-orbit coupling, *J. Chem. Phys., 61,* 3230–3239, 1974.

Dalgarno, A., The mobilities of ions in their parent gases, *Phil. Trans. R. Soc. London, Ser. A, 250,* 426–439, 1958.

Dalgarno, A., Ambipolar diffusion in the F region, *J. Atmos. Terr. Phys., 26,* 989, 1964.

Davis, C. J., Farmer, A. D., and Aruliah, A., An optimised method for calculating the O^+–O collision parameter from aeronomical measurements, *Ann. Geophys., 13A,* 541–550, 1995.

Durup, J., On long-range spin-orbit coupling effects in molecular dynamics: O_2^+ dissociation and predissociation, *Chem. Phys., 59,* 351–363, 1981.

Hickman, A. P., Huestis, D. L., and Saxon, R. P., Calculations of inelastic collisions of excited states of Xe with He and Ar, *J. Chem. Phys., 98,* 5419–5430, 1993.

Hickman, A. P. and Smith, F. T., Momentum transfer in electron–polar-molecule collisions: Results of semiclassical perturbation scattering theory, *Phys. Rev. A, 17,* 968–975, 1978.

Knof, H., Mason, E. A., and Vanderslice, J. T., Interaction energies, charge exchange cross sections, and diffusion cross sections for N^+ and O^+– O collisions, *J. Chem. Phys., 40,* 3548–3553, 1964.

Omidvar, K. and Pesnell, W. D., High-speed correction factor to the O^+– O resonance charge exchange collision frequency, *Ann. Geophys. 13,* 253–255, 1995.

Pesnell, W. D., Omidvar, K., and Hogey, W. R., Momentum transfer collision frequency of O^+– O, *Geophys. Res. Lett., 20,* 1343–1356, 1993.

Reddy, C. A., Hoegy, W. R., Pesnell, W. D., Mayr, H. G., and Hines, C. O., Accuracy of O^+– O collision cross-section deduced from ionosphere–thermosphere observations, *Geophys. Res. Lett., 21,* 2429–2432, 1994.

Salah, J. E., Interim standard for the ion-neutral atomic oxygen collision frequency, *Geophys. Res. Lett., 20,* 1543–1546, 1993.

Sharma, R., Zygelman, B., von Esse, F., and Dalgarno, A., On the relationship between the population of the fine structure levels of the ground electronic state of atomic oxygen and the translational temperature, *Geophys. Res. Lett., 21,* 1731–1734, 1994.

Stallcop, J. R., Partridge, H., and Levin, E., Resonance charge transfer, transport cross sections, and collision integrals for $N^+(^3P)$–$N(^4S_0)$ and $O^+(^4S_0)$–$O(^3P)$ interactions, *J. Chem. Phys., 95,* 6429–6439, 1991.

Stubbe, P., Frictional forces and collision frequencies between moving ion and neutral gases, *J. Atmos. Terr. Phys. 30,* 1965–1985, 1968.

A. P. Hickman, M. Medikeri-Naphade, Department of Physics, Lehigh University, Bethlehem, PA 18015. (e-mail aph2@lehigh.edu, mim8@lehigh.edu)

D. L. Huestis, Molecular Physics Laboratory, SRI International, Menlo Park, CA 94025. (e-mail huestis@sri.com)

(Received November 6, 1996; accepted November 27, 1996.)