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A new threshold energy for NO+O3→NO*2 +O2

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relaxation narrowing." It has been shown that requirements stated in motional narrowing theory can be met in the case of Mn^{2+} in cobalt salts,[5] and Gd^{3+} in non-Kramer rare earth salts,[6] at ~295 K and ~9.4 GHz. It can be shown that the requirements stated in motional narrowing theory can be met in the case of VO^{2+} doped PCSeH. Thus the observation of resolved EPR spectra of VO^{2+} in PCSeH and its broadening on lowering the temperature can be attributed to the host spin-lattice relaxation narrowing.[5–7]

The relaxation time of Co^{2+} at different temperatures has been estimated from the observed VO^{2+} impurity ion EPR linewidths when $B \parallel z$ axis in PCSeH single crystals using the expression for T_1.[5–7] Figure 2 is logarithmic graph of the estimated T_1 for the Co^{2+} when $B \parallel z$ axis as a function of temperature. It is found from the slope that $T_1 \propto T^{-n}$ where $n = 1.8$. The T_1 of Co^{2+} is found to be of the same order as observed for other cobalt salts. In the calculations, the crystallographic data of $K_2Mg(SO_4)_2 \cdot 6H_2O$ have been used. The g value is taken from $K_2Zn(SO_4)_2 \cdot 6H_2O{:}Co^{2+}$ data.[8]

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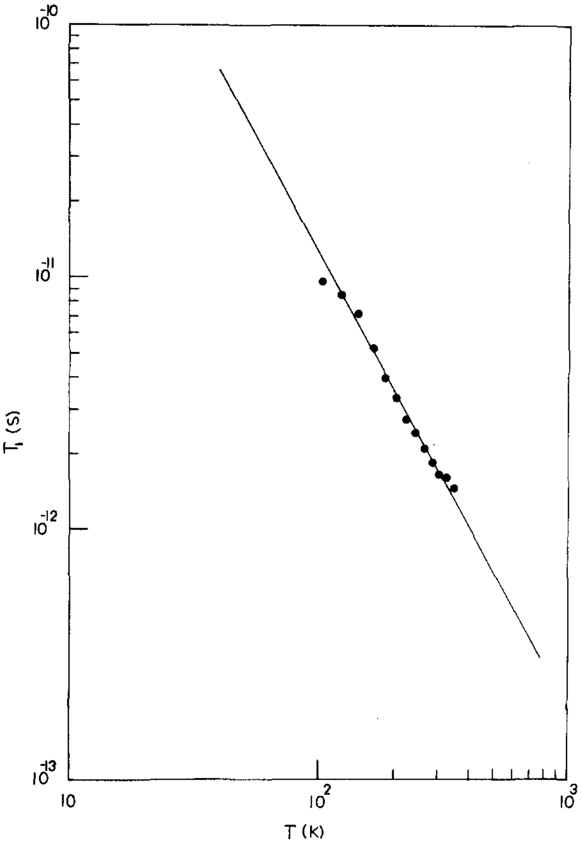

FIG. 2. Graph showing the spin-lattice relaxation time of Co^{2+} in $K_2Co(SeO_4)_2 \cdot 6H_2O$ as a function of temperature when the magnetic field is parallel to the z axis. $T \propto T^{-1.8}$. Slope $= -1.8$.

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A new threshold energy for $NO + O_3 \rightarrow NO_2^* + O_2$

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The reaction between NO and O_3 to give NO_2 and O_2 is of great atmospheric importance. Much work has been reported recently concerning the effects of collisional and reagent internal energy, as well as reagent orientation on the chemiluminescent branch of the reaction.[1–8] Two groups have previously determined the dependence of the reaction cross section on translational energy. Redpath *et al.* used a beam-scattering gas arrangement and obtained a dependence of $[(E/E_{\rm thr}) - 1]^{2.4}$ where $E_{\rm thr} = 3.2 \pm 0.3$ kcal/mol over a collision energy range of 3–6 kcal/mol.[1] van den Ende and Stolte used a supersonic-effusive crossed beam configuration and reported $\sigma \propto [E/E_{\rm thr}]^{3.75}$ where $E_{\rm thr} = 3.0 \pm 0.3$ kcal/mol over a collision energy range of 10–28 kcal/mol.[2] The work described below used a supersonic-quasieffusive crossed beam configuration for a well-defined, low energy determination of the reaction threshold. In addition, we report a very low resolution chemiluminescence spectrum recorded for four collision energies between 4.5 and 8.6 kcal/mol.

The experiments were run on a photon detection crossed molecular beam machine which has been described previously.[9] The beam source parameters are listed in Table I. A supersonic beam of NO was crossed at 90° by a quasieffusive beam of O_3, and chemiluminescence from the collision zone was focused onto a dry ice cooled RCA C31034 PMT. TOF velocity spectra of the two beams were converted to collision energy distributions, taking the finite width of the two beams into account, and interpolating as necessary to obtain distributions for nozzle temperatures at which no TOF spectra were recorded.[10,11] The collision energy range covered was 2–9 kcal/mol, with $\Delta E/E = 0.5$. The broadband wavelength spectra were recorded using a series of Bausch and Lomb narrow pass filters.

The experimental data were fit (Fig. 1) using the following functional form $\sigma \propto [1 - (E_{\rm thr}/E)]^{1.5} f(E)$, where $E_{\rm thr}$ is the threshold energy and $f(E)$ is the measured collision energy distribution. The best fit was obtained using $E_{\rm thr} = 2.0 \pm 0.2$ kcal/mol. The threshold energy and exponent were varied to obtain the best fit of the data near threshold. As can be seen in Fig. 1, the higher energy data rises faster than the fit would predict. In fact, we found it necessary to use a higher $E_{\rm thr}$ and a larger exponent to fit our high collision energy data (not shown), demonstrating the difficulty in extrapolating to zero cross section with such a steep collision energy dependence. Even near threshold, the apparent graphical threshold energy is larger than that obtained from our fit because the strong collision energy dependence skews the cross section weighted mean collision energy toward the high energy side. All of this emphasizes the importance of using the appropriate functional dependence of the cross section near threshold. While our threshold is slightly lower than those reported previously, we feel that the differences can be explained by the high sensitivity of our apparatus (reactions with $\sigma > 2\times10^{-3}$ Å^2 are detectable), by the improved collision energy resolution, and by our use of a low collision energy range eliminating the need for extrapolation to threshold.

TABLE I. Beam source parameters.

Ozone source:	
Nozzle diameter	0.38 mm
Pressure behind nozzle	13 Torr
T(nozzle)	300 K
T(beam) (calculated from TOF spectra)	200 K
Nitric oxide source:	
Nozzle diameter	0.08 mm
Pressure behind nozzle	250 Torr (pure) 400 Torr (seeded)
T(nozzle)	188–411 K
T(beam) (calculated from TOF spectra)	7–32 K

While recent work has shown that rotational energy, in particular, promotes the reaction,[12] the threshold we report is derived using only the collision energy dependence of the chemiluminescence. To obtain a better estimate of the pure translational energy threshold we must account for the internal energy present. As can be seen from Table I, contributions from O_3 vibrational energy and internal energy of NO should be negligible. Ozone rotational energy is, however, significant. Assuming an equipartition of energy in the 200

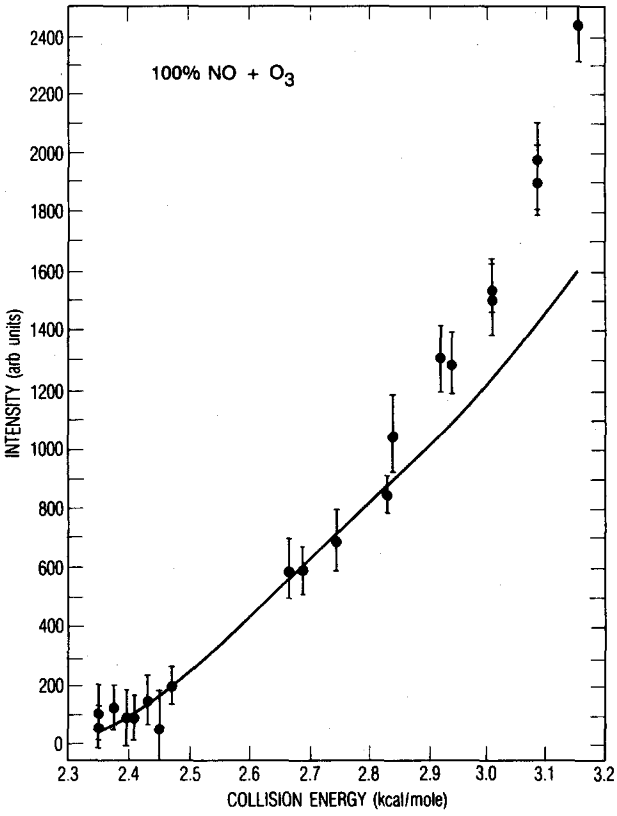

FIG. 1. Energy dependence of $NO + O_3 \rightarrow NO_2^* + O_2$ near threshold. The dots represent data points, the curve is a fit to the data given by $\sigma \propto \{1 - [(2.0 \pm 0.3)/E]\}^{1.5}$. The intensity scale is in arbitrary units while the collision energy scale is a cross section weighted mean collision energy.

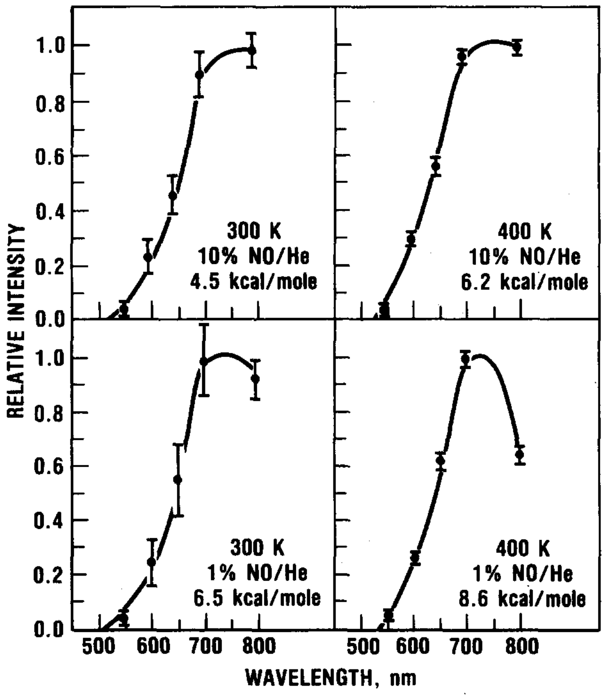

FIG. 2. Low resolution chemiluminescence spectrum of $NO + O_3 \rightarrow NO_2^* + O_2$ as a function of collision energy. The intensity for each spectrum is normalized to unit maximum. The energies reported correspond to the most probable collision energies for the energy distributions appropriate to the temperatures and NO seeding mixture used.

K beam and accounting for the relative efficiency of ozone rotational energy,[12] we estimate that the pure translational energy threshold is 2.6 ± 0.2 kcal/mol.

The chemiluminescence intensity in five broad wavelength bands was measured for the reaction at several collision energies, as shown in Fig. 2. Corrections to the wavelength spectra were made for the relative transmission of the interference filters (using measured spectral transmission for all but the 800 nm filter, for which the manufacturer's specifications were used) as well as for the wavelength response of the photomultiplier tube. We did not, however, attempt to correct for the variation of NO_2^* lifetime with wavelength. The dependence of the spectrum on collision energy contains no surprises: the change in the spectral maximum reflects the change in collision energy. The increase in collision energy apparently appears as increased internal energy in NO_2^*.

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Fine structure effect on the charge transfer reaction of $Ar^+(^2P_{3/2,1/2}) + N_2(\tilde{X}\,^1\Sigma_g^+, v=0)$

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Recently, state-specific cross-sectional data for the charge transfer reaction

$$Ar^+(^2P_{3/2}) + N_2(\tilde{X}\,^1\Sigma_g^+, v=0) \rightarrow Ar(^1S_0) + N_2^+(\tilde{X}\,^2\Sigma_g^+, v') \qquad (1)$$

at selected center-of-mass collision energies ($E_{\rm c.m.}$) have been obtained by the crossed-beam,[1,2] photoion–photoelectron coincidence,[3] and laser induced-fluorescence[4] methods. Although no potential energy surfaces (PES) have been reported for the $(Ar–N_2)^+$ system, the fact that charge transfer is the predominate product channel in $Ar^+ + N_2$ collisions over a wide $E_{\rm c.m.}$ range makes it an attractive system for a detailed theoretical investigation of charge transfer reaction dynamics. Using estimated PES for the $(Ar–N_2)^+$ system, Spalburg and Gislason[5] have performed a semiclassical calculation on reaction (1) and its reverse reaction at $E_{\rm c.m.} = 1.2$, 4.1, 10.3, and 41.2 eV. The calculated ratio of the charge transfer cross section for $Ar^+(^2P_{1/2}) + N_2(v=0)$, $\sigma_{1/2}$, to that for $Ar^+(^2P_{3/2}) + N_2(v=0)$, $\sigma_{3/2}$, when plotted as a function of $E_{\rm c.m.}$, shows a broad minimum at $E_{\rm c.m.} \approx 4.1$ eV. The observation is contrary to the previous experimental finding that $\sigma_{1/2}/\sigma_{3/2}$ is nearly independent of $E_{\rm c.m.}$.[3] The value of 0.35 for $\sigma_{1/2}/\sigma_{3/2}$ at $E_{\rm c.m.} = 8$ eV obtained by the Orsay group,[6] which was quoted in Ref. 5, is substantially lower than the value of 0.65 at $E_{\rm c.m.} = 6$ eV reported by Kato, Tanaka, and Koyano.[3] In order to provide an independent set of measurements to compare with the results of the previous experiments and to give a more vigorous test of the theoretical predictions, we have performed a state-selected study of reaction (1) in the $E_{\rm c.m.}$ range of 0.41–164.7 eV using the newly developed crossed ion–neutral beam photoionization apparatus.[7,8] Similar state-selected studies on the symmetric charge transfer reactions of $H_2^+ + H_2$[7] and $Ar^+ + Ar$[8] have been reported.

The Ar^+ reactant ions in the pure $^2P_{3/2}$ state, or at a known distribution of the $^2P_{3/2}$ and $^2P_{1/2}$ states, were prepared by photoionization of an Ar beam produced by supersonic expansion through a quartz nozzle [nozzle diameter (D_0) of 60 μm, stagnation pressure (P_0) of $\sim$80 Torr]. The pressure in the photoionization chamber was $\sim 5 \times 10^{-6}$ Torr. In a study of the charge transfer reaction $Ar^+(^2P_{3/2}) + H_2(v=0)$,[9] there was strong evidence that collisions between $Ar^+(^2P_{3/2})$ initially formed by photoionization and background Ar in the photoionization chamber gave rise to an Ar^+ beam consisting of a mixture of