

State to state rotational relaxation rate constants for CO+Ne from IR-IR double resonance experiments. Comparing theory to experiment

DAVID A. HOSTUTLER^{a)}, TONY C. SMITH and GORDON D. HAGER

*Air Force Research Laboratory/Directed Energy Directorate, 3550 Aberdeen Avenue Southeast,
Kirtland Air Force Base, New Mexico 87117-5776*

GEORGE C. MCBANE

Department of Chemistry, Grand Valley State University, Allendale, Michigan 49401

MICHAEL C. HEAVEN

Department of Chemistry, Emory University, Atlanta, Georgia 30322

^{a)}Author to whom correspondence should be addressed.

ABSTRACT

IR-IR double resonance experiments were used to study the state-to-state rotational relaxation of CO with Ne as a collision partner. Rotational levels in the range $J_i = 2-9$ were excited and collisional energy transfer of population to the levels $J_f = 2-8$ was monitored. The resulting data set was analyzed by fitting to numerical solutions of the master equation. State-to-state rate constant matrices were generated using fitting law functions. Fitting laws based on the modified exponential gap (MEG) and statistical power exponential gap (SPEG) models were used; the MEG model performed better than the SPEG model. A rate constant matrix was also generated from scattering calculations that employed the *ab initio* potential energy surface of McBane and Cybulski (J. Chem. Phys. **110**, 11734 (1999)). This theoretical rate constant matrix yielded kinetic simulations that agreed with the data nearly as well as the fitted MEG model and was unique in its ability to reproduce both the rotational energy transfer and pressure broadening data for Ne-CO. The theoretical rate coefficients varied more slowly with the energy gap than coefficients from either of the fitting laws.

I. INTRODUCTION

The CO-Ne complex has received considerable attention in the last several years. Winnewisser *et al.*¹ and Walker *et al.*² have reported pure rotational spectra of the van der Waals complex. The IR spectrum of this species has been observed by McKellar and coworkers.^{3,4} In addition to spectroscopic studies, CO+Ne has been the subject of several collisional dynamic studies. Pressure broadening^{5,6}, virial^{7,8}, transport⁹⁻¹¹ and state-to-state cross section data^{12,13} are available in the literature.

Several CO-Ne potential energy surfaces (PES) have also been presented.¹⁴⁻¹⁶ The CO-Ne complex is a good candidate for *ab initio* studies. The three heavy atoms are small enough that very high-level electronic calculations using large basis sets are not prohibitively time consuming. In 1997, Moszynski *et al.*¹⁴ presented a PES of CO-Ne using symmetry-adapted perturbation theory (SAPT). The group concluded that the complex was near T-shaped with a minimum near -54 cm^{-1} . Two more surfaces derived using the supermolecule method were published in 1999. The first, by McBane and Cybulski,¹⁵ used a large basis set at the CCSD(T) level of theory. It did not describe the ground state structure of Ne-CO as well as the SAPT potential, but comparisons to the scattering data indicated that it described the repulsive part of the interaction better than SAPT. The second surface, reported that year by Subramanian *et al.*,¹⁶ used a smaller basis set than McBane and Cybulski and the MP4 level of theory. This group did not report an analytical fit and did not comment on the agreement with experimental results.

Our group is currently measuring state-to-state rotational relaxation rate constants for CO with various collision partners using IR-IR double resonance experiments. This is the third project in a series; results for CO+CO¹⁷ and CO+He¹⁸ have already been presented. This paper describes our CO+Ne double resonance data and modeling. After the data were collected, the

full rotational relaxation rate constant matrix was approximated by computer simulations of our data using the master equation and two common fitting laws: the modified exponential gap (MEG) and the statistical power exponential gap (SPEG) models. Additionally, purely theoretical rate constants determined from the CCSD(T) potential energy surface of McBane and Cybulski¹⁵ were compared to both our kinetics data and to CO+Ne pressure broadening data.

II. EXPERIMENT

Because it is sensitive to individual rate constants, the pump-probe double resonance technique¹⁹ is useful for monitoring rotational energy transfer (RET). Our experiment was carried out in a 296 K gas cell containing 0.25 torr of CO (Air Products, UHP) and 0.50 torr of Ne (Spectra Gases, UHP). During the experiment a pump laser pulse, which was resonant with a selected transition of the first overtone band (2-0), prepared a population of molecules in a single rovibrational level of CO ($\nu = 2$). Since the vibrational frequency of carbon monoxide is large, the initial thermal population in $\nu = 2$ is negligible so that clean population of a single vibration-rotation level could be achieved. A continuous wave (cw) probe laser was tuned to various transitions of the (3-2) absorption band. As RET processes redistributed the population within the CO ($\nu = 2$) rotational manifold the time-dependent transmittance of the probe laser was recorded as our double resonance signal. Details of the IR-IR pump-probe apparatus and procedure have been described elsewhere^{17,18} and will not be repeated here.

III. RESULTS

A. Data Reduction

The raw pump-probe data is influenced by more than just the rotational relaxation. The two other factors that contribute to the observed transient absorption signals are vibrational relaxation and velocity relaxation. Our earlier papers^{17,18} describe the approach we use to remove those effects from the transient absorption signals, converting each trace into a “population profile” $P(J_i, J_f, t)$ that is proportional to the time-varying population in level J_f that would be observed after excitation of level J_i if no vibrational relaxation was taking place. The population profiles are normalized so that the long-time asymptote of each corresponds to the population in J_f at 296 K rotational equilibrium.

Data were collected for 49 different J_i, J_f pairs, with $2 \leq J_i \leq 9$ and $2 \leq J_f \leq 8$. To make the data more manageable each population profile was fit to the expression

$$\bar{P}(J_i, J_f, t) = a \left[1 - \exp(-bt) - \frac{c}{c+d} \left(1 + \frac{b \exp[-(c+d)t] - \exp(-bt)(c+d)}{c+d-b} \right) \right] \quad (1)$$

where a , b , c , and d are adjustable parameters. The values for the fitted parameters for each of the profiles are given in Table I.

B. Simulation of Rotational Relaxation Kinetics with empirical RET models

Rotational relaxation in $v = 2$ was simulated using a system of coupled differential equations (the master equation) of the form:

$$\frac{dN_J}{dt} = \sum_{J'} (k_{J \leftarrow J'}^{CO-CO} N_{J'} - k_{J' \leftarrow J}^{CO-CO} N_J) [CO] + \sum_{J'} (k_{J \leftarrow J'}^{CO-Ne} N_{J'} - k_{J' \leftarrow J}^{CO-Ne} N_J) [Ne] \quad (2)$$

where N_J is the population in the J level, and $k_{J \leftarrow J'}^{CO-CO}$ and $k_{J \leftarrow J'}^{CO-Ne}$ are the CO+CO and CO+Ne rotational relaxation rate constants, respectively. Values for the CO+CO rate constants ($k_{J \leftarrow J'}^{CO-CO}$) were taken from the previous work of Phipps et. al.¹⁷

The master equation properly incorporates all rotational levels. However, only those rotational levels that contain significant thermal populations need to be included to provide an accurate description of rotational relaxation. Since $\sim 97\%$ of the rotational population resides in rotational levels below $J < 20$ at 297 K we restricted the model to consider $J \leq 29$. A matrix of 900 rate constants was then needed to specify the system of equations. Applying detailed balance and setting the diagonal elastic rates to zero reduces the problem to that of finding 435 independent rate constants, but this is still too many parameters to be determined from the data collected in these experiments. Therefore, we have applied the usual method of representing the CO+Ne rotational-translation relaxation rate constant matrix with fitting law functions.

The full CO+Ne rotational relaxation rate constant matrix was extracted using two common fitting laws: the modified exponential gap (MEG)²⁰⁻²² and statistical power exponential gap (SPEG)²¹⁻²³ models. Our previous CO+CO RET paper gives a detailed description of our technique and procedure for using these fitting laws.¹⁷ For upward transitions ($j > i$), the MEG law had the form:

$$k_{j \leftarrow i} = \alpha \cdot \exp\left(\frac{-\beta \Delta E_{ji}}{kT}\right) \cdot \left(\frac{1 + \frac{2E_i}{\gamma kT}}{1 + \frac{2E_i}{kT}}\right)^2 \quad (3)$$

and the SPEG law was expressed as:

$$k_{j \leftarrow i} = \alpha \cdot \exp\left(\frac{-\beta \Delta E_{ji}}{kT}\right) \cdot \left(\frac{\Delta E_{ji}}{B_{v=2}}\right)^{-\gamma} \quad (4)$$

where α , β , and γ are the adjustable parameters in each case. The rate coefficients for downward transitions ($j < i$) were obtained by detailed balance.

The master equation was solved numerically using the fourth order Runge-Kutta method and the MEG and SPEG fitting law expressions were fitted to the $\bar{P}(J_i, J_f, t)$ curves. A computer program was written that independently varied the adjustable fitting parameters for each of the fitting laws to minimize the sum of the squared deviations (SSD). The program terminated when the sum of squared deviations (SSD) between the master equation solutions and the $\bar{P}(J_i, J_f, t)$ curves, sampled at 100 points between 0 and 4 μ s, reached a minimum.

The resulting values for the best-fit parameters from computer simulations of our CO+Ne data set, using the MEG and SPEG models, are given in Table II. The MEG computer simulations reproduced the experimentally determined $P(J_i, J_f, t)$ data better than the SPEG model, with a 43% decrease in the SSD between the computer simulations and the reduced experimental data. Fig. 1 shows simulations using the MEG model (solid line) for a series of population profiles with $J_i = 8$ and $2 \leq J_f \leq 7$. The asymptotic values of the data and the fitted curves in Fig. 1 are equal to the equilibrium populations. The information in the comparison is therefore in the initial slope of the fitted profile and the shape of its approach to equilibrium. The simulations using the MEG model reproduce our CO+Ne kinetics data very well with most of the simulation traces within the experimental noise.

C. *Ab initio* rate coefficients

We also calculated the matrix of RET rate coefficients directly from an *ab initio* model of the Ne-CO potential energy surface. Since the experiment was carried out with CO in $\nu = 2$, it would be best to use a potential surface averaged over the $\nu = 2$ vibrational motion of CO. However, none of the existing Ne-CO potential surface models includes the CO vibrational coordinate. In comparisons to the results from scattering studies,^{12,13} the CCSD(T) surface of McBane and Cybulski appeared to give a better description of the repulsive wall, so we selected it for simulation of the double resonance data.

Time independent coupled channel scattering calculations were carried out with the MOLSCAT program of Hutson and Green²⁴. The “S2” potential surface of McBane and Cybulski was used to describe the intermolecular potential. That surface treats CO as a rigid rotor with a C-O internuclear distance equal to the diatomic potential minimum. The asymptotic rotational energy levels used in the calculation were those of free CO in $\nu = 2$. The $\nu = 2$ rotational constants were obtained from the work of Maki, Wells, and Jennings.²⁵ The two-dimensional potential was expanded using 16 Legendre polynomial terms with radially dependent expansion coefficients.

The close coupled equations were solved using the hybrid log derivative Airy propagator of Alexander and Manolopolous.²⁶ Close coupled (CC) calculations were performed for all total energies below the $J = 21$ threshold (870 cm^{-1}), and in a few instances for energies up to 1500 cm^{-1} . The rotational basis sets included all open channels and at least two closed channels. Most calculations at energies above 870 cm^{-1} used the coupled states (CS) approximation of McGuire and Kouri²⁷, and the basis sets then included at least one closed channel. All propagations were carried out to a center of mass separation of at least 28 \AA , though many calculations were

extended to larger distances to ensure that the asymptotic boundary conditions were imposed beyond the centrifugal barrier. The partial wave sum was terminated when the elastic cross sections had converged to at least 1 \AA^2 and the inelastic cross sections to 0.01 \AA^2 . At the highest energies in our calculations (2182 cm^{-1}), the maximum total angular momentum included in the partial wave sum was $179\hbar$.

The grid of energies used in the calculations was selected to capture most of the variations in cross sections just above the energy thresholds for channel openings for the purpose of thermal averaging. Just above each threshold, beginning with $J = 1$, a series of total energies was used whose spacings began at 1 cm^{-1} and increased to larger values as the cross sections became smoother. Each series was terminated when the next threshold was reached.

Calculations were only performed for the dominant ^{20}Ne isotope. Test calculations at a few energies indicated that inclusion of the minor ^{22}Ne isotope would modify the calculated rate coefficients by less than 1%.

C.2 Thermal averaging

Thermally averaged cross sections were evaluated according to the expression

$$\sigma_{if}(T) = (kT)^{-2} \int_0^{\infty} \varepsilon_i \sigma_{if}(\varepsilon_i) \exp(-\varepsilon_i / kT) d\varepsilon_i \quad (5)$$

where ε_i is the pre-collision center-of-mass translational energy. The integration was carried out using the trapezoidal rule, and the cross section was assumed to be zero for all translational energies above the highest in our computed set. The truncation of the integral introduces negligible error for rate coefficients involving only $J < 21$. For higher rotational levels, truncation causes a systematic underestimation of the rate coefficients. The thermalized cross

sections were multiplied by the average collision speed, $\langle v \rangle = (8kT/\pi\mu)^{1/2}$, to convert them to state-to-state rate coefficients.

The CCSD(T) *ab initio* rate constants were inserted into the master equation, which was then solved to simulate the population evolutions. Fig. 2 shows a comparison of the experimental curves and computer simulations using the rate matrices generated from the CCSD(T) potential energy surface and the MEG model. In the figure the CCSD(T) predicted populations are represented by the smooth curves through the $\bar{P}(J_i, J_f, t)$ data while the MEG simulations are represented by solid points. The agreement between the CCSD(T) theoretical rate constant matrix model and the experimental data was very favorable, with a SSD of 0.172, as listed in Table II.

IV. DISCUSSION

Graphical representations of the CO+Ne rate constant matrices from the MEG, SPEG, and CCSD(T) models are shown in Figs. 3a, 3b, and 3c. The CCSD(T) and MEG rate constant histograms are very similar in shape. Computer simulations using these rate constant matrices were found to reproduce the experimental data much more accurately than the SPEG model. The most distinctive feature of the CCSD(T) and MEG rate matrices is that the rate constants near the diagonal have a weak dependence on the energy gap. The opposite is true for the SPEG model. The rate constant matrix generated from the SPEG fitting law function is much more dependent on the energy gap and overestimates the low J rate coefficients while underestimating higher J coefficients.

A good test of the overall quality of these CO+Ne rate constant matrices is to see how well they perform when used to simulate pressure broadening linewidth data. Therefore, we have

used each of these rate constant matrices to predict the CO+Ne pressure broadening data of Bouanich.²⁸ During these simulations, we assumed that the major contributor to the pressure broadening linewidths was rotationally inelastic collisions (the diagonal rate constants ($k_{J \leftarrow J}^{CO-Ne}$) were set to zero) and that the RET rate constants were vibrationally independent. The pressure broadening coefficients are then given by²⁹

$$\gamma(J', J'') = \frac{1}{4\pi} \left(\sum_{J_f'} k_{J_f' \leftarrow J'} + \sum_{J_f''} k_{J_f'' \leftarrow J''} \right) \quad (6)$$

where J' and J'' are the upper and lower J values for a specific rovibrational line. Pressure broadening coefficients calculated from the CCSD(T), MEG and SPEG rate constant matrices are compared with the experimental data of Bouanich²⁷ in Fig. 4. The CCSD(T) *ab initio* rate constant matrix (solid gray circles) reproduced the experimental data (black solid circles) much better than the rate matrices generated from the MEG or SPEG fitting laws. The experimental data and the CCSD(T) predicted pressure broadening linewidths both have only a weak J dependence. The pressure broadening coefficients generated from the MEG rate matrix are slightly more J -dependent than those produced from the CCSD(T) potential energy surface but the values are too small. The pressure broadening coefficients generated from the SPEG fitting law rate matrix compare poorly to the experimental data. This model overestimates the coefficients for low values of J and underestimates in the intermediate J range. The CCSD(T) rate matrix compares most favorably with both the kinetics and the pressure broadening data. The complete CCSD(T) rate constant matrix for values of $J \leq 20$ is listed in Table III.

In our recent study of CO+He rotational relaxation¹⁸ using pump-probe double resonance, we generated the CO+He rate constant matrix from the symmetry adapted perturbation theory (SAPT) potential energy surface of Heijmen et al.³⁰ The SAPT rate constant matrix reproduced

both the CO+He kinetics and pressure broadening data very well. The CO+He room temperature pressure broadening data is almost J -independent, revealing only a weak dependence on the energy gap.¹⁸ As indicated by the rate constants along the diagonal of each matrix, the CCSD(T) rate constant matrix for CO+Ne (shown in Fig. 3c) is slightly more dependent on the energy gaps than the CO+He SAPT rate matrix (Fig. 3d). It appears that a weak dependence of the energy transfer rate constants on the energy gaps is a characteristic of impulsive collisions where the dominant interaction between the collision pair occurs at short range, on the repulsive wall of the intermolecular potential. The slightly greater dependence of the CO+Ne rate constants on the energy gaps, as compared to CO+He, is consistent with the fact that the slower CO+Ne collisions are not as impulsive, and the long-range attraction between the collision pair is greater. The inelastic cross sections for Ne-CO collisions are larger than the corresponding He cross sections; for example, the $3 \rightarrow 8$ cross section at 210.55 cm^{-1} is 1.39 \AA^2 for He and 3.35 \AA^2 for Ne. However, the larger cross sections are compensated by the higher He-CO collision rate, so that the room temperature CO+Ne rotational relaxation rate constants are slightly slower than those of CO+He.

The rate coefficients for transitions with small to moderate values of $|\Delta J|$ generated from the CO+Ne CCSD(T) *ab initio* potential show a small preference for transitions with odd values of ΔJ . This trend is illustrated in Fig. 5 where the rate constants for transfer from $J_i=5$ and 10 are plotted as a function of J_f . The propensity for odd ΔJ transitions survives the thermal averaging because it holds for a broad range of collision energies. A propensity for odd ΔJ transitions was also observed in the CO+He rate constant matrix, generated from the SAPT potential energy surface, but there the degree of modulation was more pronounced. Conversely, the data for CO+CO RET collisions exhibits a preference for even ΔJ transitions. These symmetry

propensities reflect the symmetry properties of the intermolecular potentials over the range of intermolecular separations that are most important for the energy transfer processes. Hence, the even ΔJ preference of CO+CO reflects the symmetry of the interaction over both the repulsive and attractive parts of the surface, since they both contribute importantly to the rotational energy transfer. CO-He and CO-Ne rotational relaxation are both dominated by dynamics on the repulsive wall, and the shape of that wall produces odd ΔJ propensities in both cases. Unfortunately we have not been able to obtain experimental confirmation of these trends from the RET data for He and Ne collisions. In our experiments the odd ΔJ transitions for CO+He or Ne are masked by the even ΔJ propensity of the concurrent CO+CO collisions.

V. SUMMARY

Time-resolved pump-probe measurements were used to examine CO+Ne rotational energy transfer within the CO $\nu = 2$ rotational manifold. Rotational levels in the range $J_i = 2-9$ were excited and transfer of population to the levels $J_f = 2-8$ was monitored. The resulting data set was analyzed by fitting to numerical solutions of the master equation. State-to-state rate constant matrices were generated using fitting law functions and *ab initio* theoretical calculations that employed a CCSD(T) potential energy surface.¹⁵ The MEG fitting law and the theoretical rate constants yielded acceptable simulations of the kinetic data. However, only the latter were able to reproduce both the kinetic data and the pressure broadening coefficients for CO+Ne. In this respect the conclusions of the present work are closely aligned to those derived from our recent work on CO+He. Again we find that correlations in fitting rate constant matrices to RET kinetics or pressure broadening data alone can be greatly reduced when a simultaneous fit to both data sets is required. For both CO+Ne and CO+He the best rate constant matrices were obtained

from high-level theoretical calculations, rather than empirical fitting procedures. The present study shows that current *ab initio* computational methods are capable of predicting the thermally averaged dynamics of CO+Ne with near quantitative accuracy.

ACKNOWLEDGMENTS

We are grateful to the Air Force Office of Scientific Research (AFOSR) for support of this research. Authors T.C.S. and D.A.H. would like to thank the National Research Council for postdoctoral fellowships. M.C.H. thanks AFOSR for support through grant AFOSR F49620-02-1-0357.

REFERENCES

1. G. Winnewisser, B. S. Dumesh, I. Pak, L. Surin, F. Lewen, D. A. Roth, and F. S. Rusin, *J. Mol. Spectrosc.*, **192**, 243 (1998).
2. K. A. Walker, T. Ogata, W. Jager, M. C. L. Gerry, and I. Ozier, *J. Chem. Phys.*, **106**, 7519 (1997).
3. R. W. Randall, A. J. Cliffe, B. J. Howard, and A. R. W. McKellar, *Mol. Phys.*, **79**, 1113 (1993).
4. A. R. W. McKellar and M. C. Chan, *Mol. Phys.*, **93**, 253 (1998).
5. R. B. Nerf Jr., and M. A. Sonnenberg, *J. Mol. Spectrosc.*, **58**, 474 (1975).
6. A. Henry, D. Hurtmans, M. Margottin-Maclou, and A. J. Valentin, *J. Quantum Spectrosc. Rad. Transfer*, **56**, 647 (1996).
7. R. Moszynski, T. Korona, T. G. A. Heijmen, P. E. S. Wormer, A. van der Avoird, and B. Schramm, *Polish J. Chem.*, **72**, 1479 (1998).
8. K. Vatter, H. J. Schmidt, E. Elias, and B. Schramm, *Ber. Bunsen-Ges. Phys. Chem.*, **100**, 73, (1996).
9. J. Kestin, S. T. Ros, and W. A. Wakeham, *Ber. Bunsen-Ges. Phys. Chem.*, **86**, 753 (1982).
10. R. D. Trengrove, H. L. Robjohns, and P. J. Dunlop, *Ber. Bunsen-Ges. Phys. Chem.*, **88**, 450 (1984).
11. N. Imaishi and J. Kestin, *J. Phys. A.*, **126**, 98, (1984).
12. S. Antonova, A. Lin, A. P. Tsakotellis, and G. C. McBane, *J. Chem. Phys.*, **110**, 11742 (1999).
13. K. T. Lorenz, D. W. Chandler, and G. C. McBane, *J. Phys. Chem. A*, **106**, 1144 (2002).
14. R. Moszynski, T. Korona, P. E. S. Wormer, and A. van der Avoird, *J. Phys. Chem. A*, **101**, 4690 (1997).
15. G. C. McBane and S. M. Cybulski, *J. Chem. Phys.*, **110**, 11734 (1999).
16. V. Subramanian, K. Chitra, D. Sivanesan, R. Amutha and S. Sankar, *Chem. Phys. Lett.*, **307**, 493 (1999).

17. S. P. Phipps, T. C. Smith, G. D. Hager, M.C. Heaven, J. K. McIver and W.G. Rudolph, *J. Chem. Phys.* **116**, 9281 (2002).
18. T. C. Smith, D. A. Hostutler, G. D. Hager, M. C. Heaven and G. C. McBane, "State-to-State Rotational Rate Constants of CO+He : Simulation of the Infrared Double Resonance Data Using the SAPT Theoretical PES." *J. Chem. Phys. Manuscript Submitted* (2003).
19. (a) J. J. Klaassen, S. L. Coy, J. I. Steinfeld and B. Abel, *J. Chem. Phys.* **101**, 10533 (1994); (b) J. J. Klaassen, S. L. Coy, J. I. Steinfeld and Ch. Roche, *J. Chem. Phys.* **100**, 5519 (1994); (c) C. C. Flannery, J. I. Steinfeld and R. R. Gamache, *J. Chem. Phys.* **99**, 6495 (1993).
20. M. L. Koszykowski, L.A. Rahn, R. E. Palmer and M.E. Coltrin, *J. Phys. Chem.* **91**, 41 (1987).
21. J. P. looney, G. J. Rosasco, L. A. Rahn, W. S. Hurst and J. W. Hahn, *Chem. Phys. Lett.* **161**, 232 (1989).
22. J. I. Steinfeld, P. Ruttenberg, G. Millot, G. Fanjoux and B. Lavorel, *J. Phys. Chem.* **95**, 9638 (1991) and references therein.
23. B. C. Sanctuary, *Chem. Phys. Lett.* **62**, 378 (1979).
24. J. M. Hutson and S. Green, MOLSCAT V. 14., distributed by Collaborative Computational Project No. 6 of the Engineering and Physical Sciences Research Council (UK), 1994.
25. A. G. Maki, J. S. Wells, and D. A. Jennings, *J. Mol. Spectrosc.* **144**, 224 (1990).
26. M. H. Alexander and D. E. Manolopoulos, *J. Chem. Phys.* **86**, 2044 (1987).
27. P. McGiure and D. J. Kouri, *J. Chem. Phys.* **60**, 2488 (1974).
28. J. -P. Bouanich, *J. Quant. Spectrosc. Radiat. Transfer*, **12**, 1609 (1972).
29. J. I. Steinfeld and R. R. Gamache, *Spectrochimica Acta* **54A**, 65 (1998).
30. T. G. A. Heijmen, R. Moszynski, P. E. S. Wormer, and A. van der Avoird, *J. Chem. Phys.* **107**, 9921 (1997).

Figure Captions

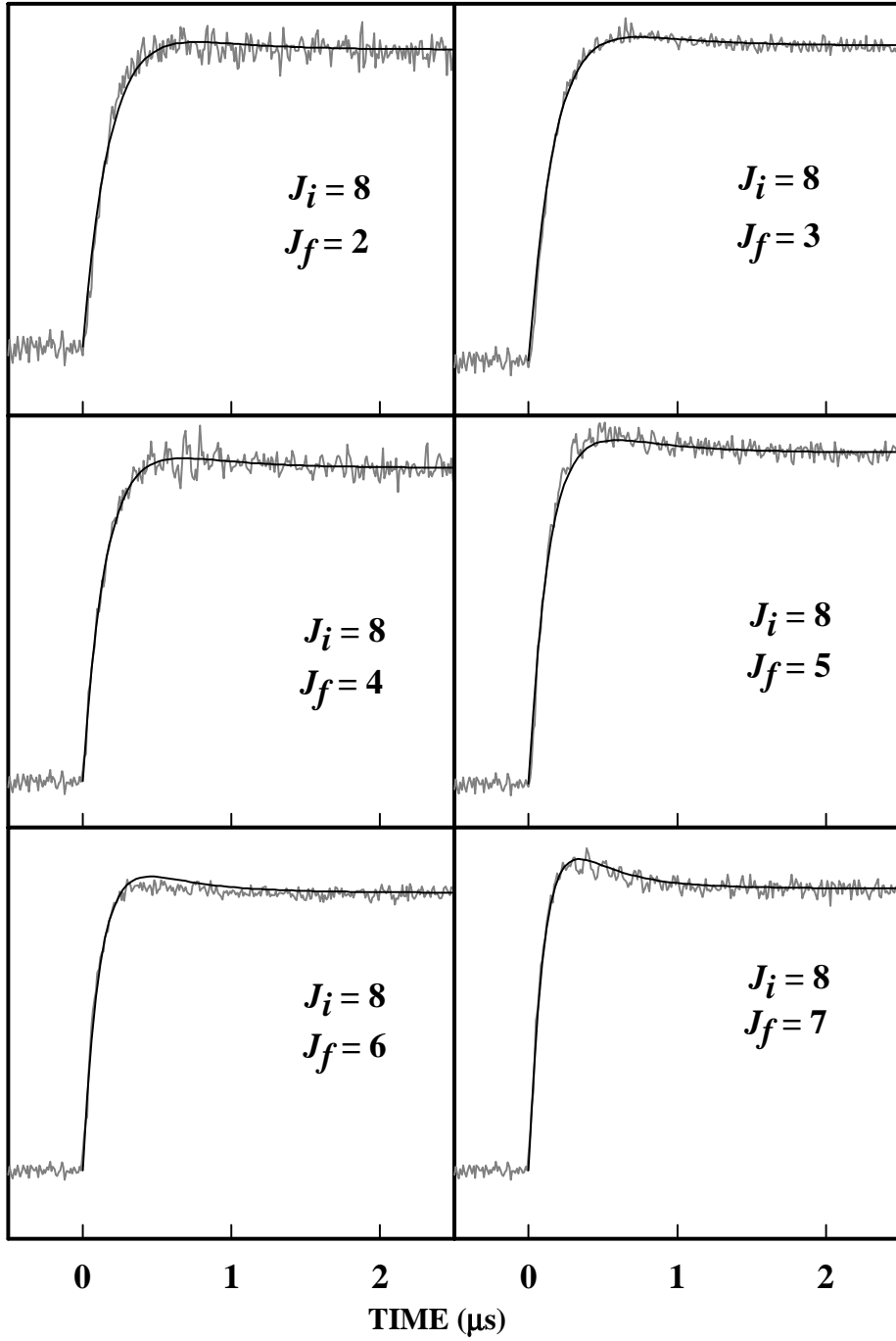
FIG. 1. Time-dependent rotational populations for $J_f = 2$ to 7 following the excitation of $J_i = 8$. The smooth lines through the data are from computer simulations that used rate constants represented by the MEG fitting law model.

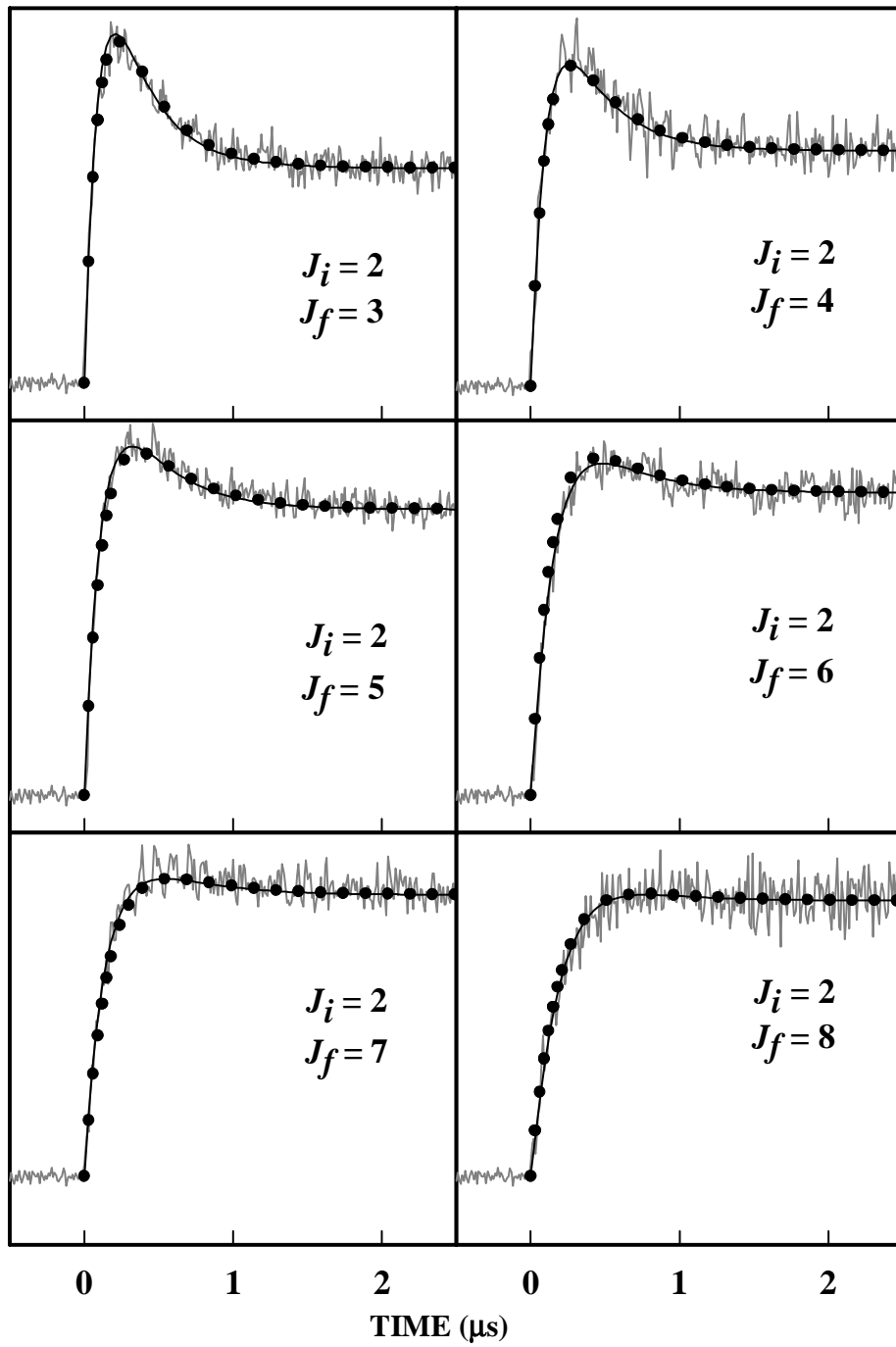
FIG. 2. Time-dependent rotational populations for $J_f = 3$ to 8 following the excitation of $J_i = 2$. The figure also includes computer simulations of the CO+Ne data using rate constants derived from the CCSD(T) potential energy surface¹⁵ (solid lines) and rate constants represented by the MEG fitting law model (solid points).

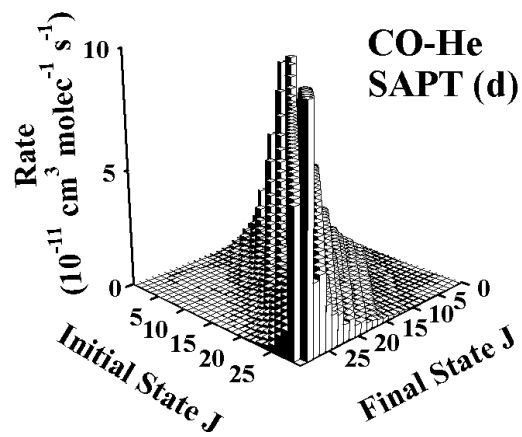
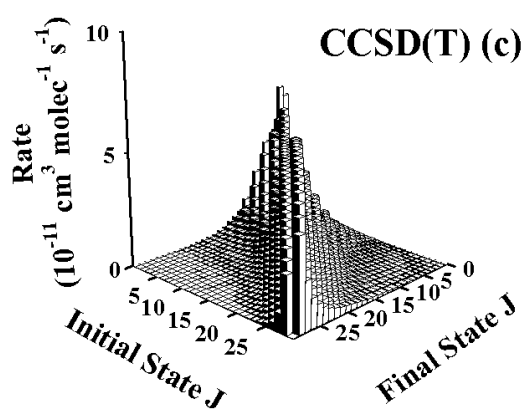
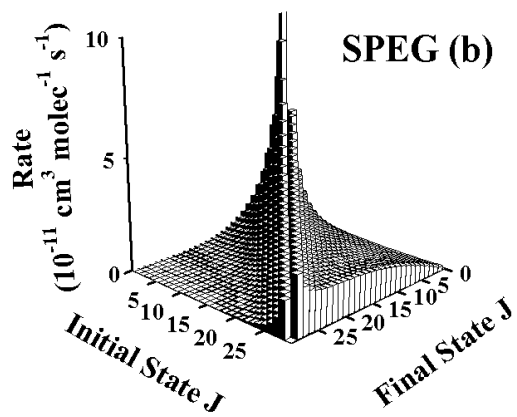
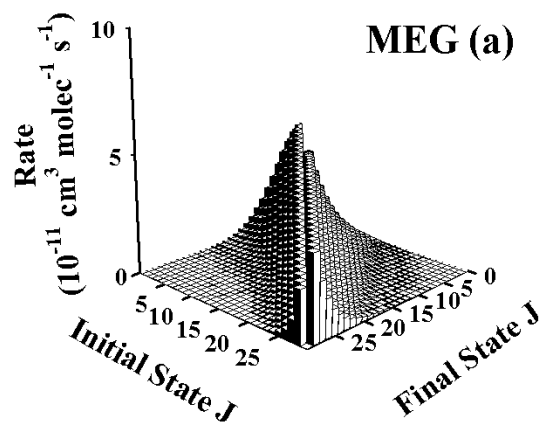
FIG. 3. Bar graph representations of rate constant matrices generated from the MEG, SPEG, and CCSD(T) models are displayed in plots *a*, *b*, and *c*, respectively. Rate constants predicted from the CO-He SAPT potential energy surface³⁰ are displayed in plot *d*.

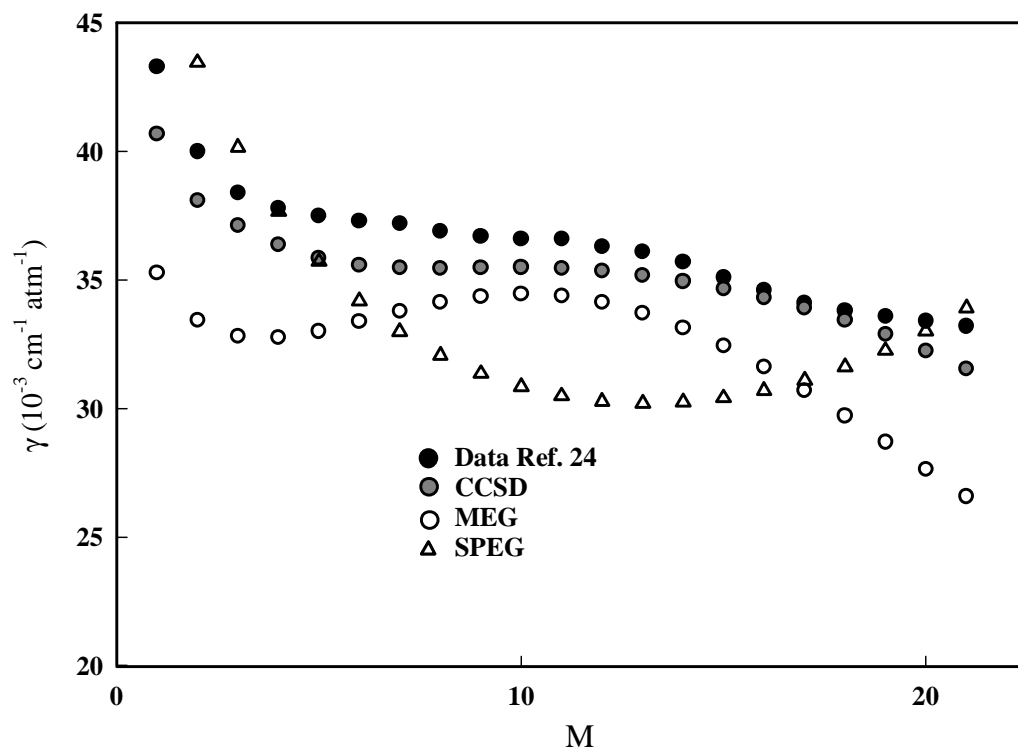
FIG. 4. Simulations of the CO-Ne pressure broadening data using the predictions for the CCSD(T) potential energy surface, and the MEG and SPEG fitting law models. Positive values of M indicate R branch lines with $J = M - 1$. The experimental CO-Ne pressure broadening data was taken from Ref. 28 and is illustrated by the solid black circles. The predictions from the CCSD(T) PES are represented by gray solid circles and the MEG and SPEG fitting laws are represented by open circles and triangles respectively.

FIG. 5. Rate constants derived from the CCSD(T) potential energy surface. The solid points and open circles correspond to $J_i = 5$ and 10, respectively. The maximum in the Boltzmann distribution occurs at $J = 7$. Hence the rate constants for $J_i = 5$ favor upward transfer while those for $J_i = 10$ favor downward transfer. The rate constants show a weak preference for odd ΔJ transitions.









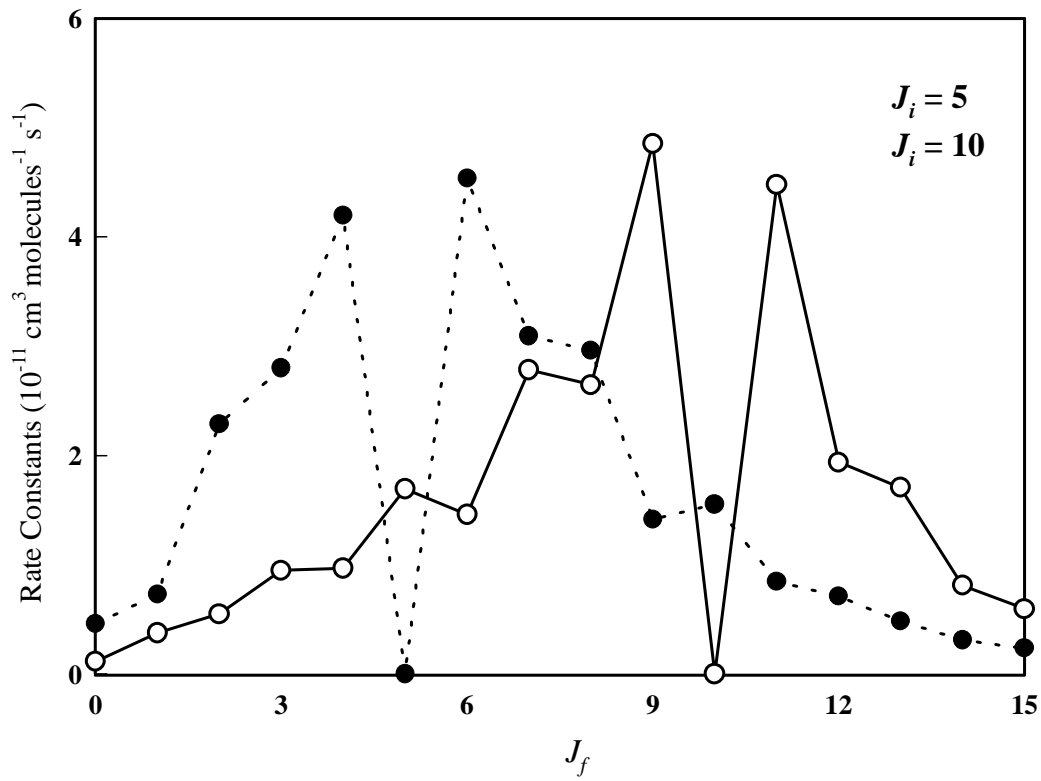


Table I. Coefficients for Eq.(1) which represents the time-dependent population profiles.

J_i	J_f	a^a	b^b	c^b	d^b	J_i	J_f	a	b
2	3	40.7087	0.003157	0.008915	0.001454	6	2	7.9313	0.004321
2	4	33.6912	0.003180	0.006295	0.001599	6	3	25.7596	0.002253
2	5	41.6091	0.002370	0.007003	0.001568	6	4	19.1714	0.004083
2	6	14.8988	0.004422	0.002035	0.002401	6	5	10.9019	0.009707
2	7	39.0913	0.001661	0.005145	0.001362	6	7	11.6403	0.008241
2	8	11.9187	0.003473	0.001189	0.002443	6	8	10.0222	0.008170
3	2	24.0438	0.003633	0.007645	0.001669	7	2	7.4221	0.005823
3	4	35.1349	0.003197	0.007151	0.001724	7	3	8.6747	0.004714
3	5	42.3232	0.002716	0.007693	0.001687	7	4	9.0656	0.007182
3	6	35.3386	0.002443	0.006249	0.001847	7	5	10.1692	0.008640
3	7	20.4064	0.002772	0.002972	0.001991	7	6	10.5340	0.009746
3	8	11.6978	0.003717	0.001196	0.002606	7	8	11.0607	0.009091
4	2	24.0690	0.003272	0.007803	0.001701	8	2	6.4718	0.004599
4	3	33.9443	0.003113	0.008081	0.001634	8	3	14.6834	0.002628
4	5	45.4953	0.002903	0.008267	0.001661	8	4	16.8941	0.002728
4	6	34.8549	0.002880	0.005981	0.001800	8	5	9.0525	0.007559
4	7	40.5052	0.001957	0.006537	0.001655	8	6	12.4743	0.006527
4	8	12.6836	0.004011	0.001476	0.002537	8	7	11.1232	0.009401
5	2	16.5485	0.003222	0.005627	0.001981	9	2	5.5131	0.004922
5	3	30.1540	0.002625	0.007466	0.001744	9	3	7.9630	0.003594
5	4	34.7144	0.002831	0.007562	0.001850	9	4	9.1640	0.004259
5	6	36.9941	0.002923	0.007334	0.002044	9	5	11.5296	0.003863
5	7	31.6740	0.002841	0.006345	0.002212	9	6	26.7508	0.002409
5	8	24.7787	0.002651	0.004796	0.002293	9	7	12.9511	0.006608
						9	8	11.0695	0.009529

^aParameter has units of number density (molecules cm⁻³). Sufficient digits are quoted to reproduce data to full accuracy.

^bParameters have units of ns⁻¹.

Table II. Experimentally determined parameters for the MEG and SPEG fitting laws and the variance between computer simulations and our experimental data.

Parameters	Fitting Results ^a		Theoretical Results
	MEG	SPEG	CCSD(T)
$\alpha/(10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$	4.51(48)	18.1(3.0)
β	1.73(19)	0.77(15)
γ	1.08(16)	0.502(40)
SSD ^b	0.152	0.267	0.172

^aExperimental values from this work. Values in parentheses are estimated errors, which were obtained by varying the parameter until a 10% increase in the SSD was obtained while holding all other parameters constant.

^bSum of squared deviations between experimental and computer simulated population profiles.

Table III. Theoretical CO-Ne inelastic rotational relaxation rate constants calculated from the CCSD(T) PES.

$J_i \setminus J_f$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
0	0.00	1.98	1.33	0.68	0.34	0.46	0.17	0.28	0.13	0.16	0.11	0.10	0.09	0.06	0.06	0.05
1	5.83	0.00	3.26	2.26	1.66	0.73	1.11	0.45	0.65	0.37	0.37	0.29	0.23	0.22	0.16	0.15
2	6.27	5.24	0.00	3.79	2.63	2.29	0.99	1.47	0.68	0.85	0.55	0.50	0.42	0.32	0.31	0.23
3	4.29	4.82	5.03	0.00	4.06	2.80	2.62	1.19	1.64	0.85	0.95	0.67	0.57	0.51	0.37	0.36
4	2.53	4.23	4.16	4.86	0.00	4.20	2.88	2.77	1.33	1.69	0.97	0.99	0.75	0.60	0.56	0.41
5	3.83	2.07	4.04	3.73	4.68	0.00	4.29	2.88	2.81	1.42	1.69	1.03	0.99	0.79	0.61	0.57
6	1.51	3.33	1.85	3.70	3.40	4.54	0.00	4.40	2.82	2.81	1.46	1.66	1.07	0.97	0.81	0.61
7	2.53	1.36	2.79	1.71	3.32	3.09	4.47	0.00	4.54	2.74	2.78	1.47	1.59	1.08	0.92	0.80
8	1.17	1.95	1.25	2.29	1.56	2.96	2.80	4.44	0.00	4.70	2.65	2.73	1.47	1.51	1.09	0.87
9	1.34	1.04	1.50	1.13	1.88	1.41	2.65	2.54	4.45	0.00	4.85	2.56	2.66	1.46	1.42	1.08
10	0.85	0.97	0.89	1.16	0.99	1.55	1.26	2.37	2.31	4.47	0.00	5.00	2.48	2.57	1.47	1.33
11	0.65	0.69	0.72	0.74	0.91	0.85	1.28	1.12	2.13	2.11	4.48	0.00	5.14	2.42	2.47	1.47
12	0.51	0.47	0.54	0.54	0.60	0.71	0.72	1.06	1.00	1.91	1.94	4.49	0.00	5.27	2.38	2.36
13	0.32	0.38	0.34	0.41	0.41	0.48	0.56	0.61	0.88	0.90	1.71	1.80	4.49	0.00	5.39	2.36
14	0.26	0.23	0.28	0.25	0.31	0.31	0.39	0.43	0.52	0.72	0.81	1.52	1.68	4.48	0.00	5.50
15	0.15	0.18	0.16	0.20	0.19	0.23	0.24	0.31	0.34	0.45	0.60	0.74	1.36	1.59	4.46	0.00
16	0.11	0.11	0.12	0.12	0.14	0.14	0.17	0.18	0.24	0.27	0.38	0.49	0.67	1.20	1.53	4.43
17	0.07	0.07	0.08	0.08	0.09	0.10	0.10	0.13	0.14	0.19	0.22	0.32	0.42	0.62	1.07	1.48
18	0.05	0.05	0.05	0.05	0.05	0.06	0.07	0.08	0.09	0.11	0.15	0.18	0.27	0.35	0.56	0.96
19	0.03	0.03	0.03	0.03	0.03	0.04	0.04	0.05	0.06	0.07	0.09	0.12	0.15	0.23	0.31	0.51
20	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.03	0.03	0.04	0.05	0.07	0.09	0.12	0.19	0.27

Rate constants in units of $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.