

Critical Analysis of Conflicting Data: Previous Evaluations

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Data collections and critical data evaluations are not the same !

Critical data evaluations require:

groups of true experts

(experience !)

experimentalists

(with appreciation of theoretical models)

theoreticians

(with appreciation of experimental relevance)

users

(if possible, indicating fields of interest)

some money, more devotion

difficult to realize

(because of very little support)

Examples:

- (i) IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry (starting as a CODATA task group 1978, enduring until present
Atkinson, Baulch, Cox, Crowley, Hampson, Hynes, Jenkin, Rossi, Troe,
new members: Ammann and Wallington)

New evaluations in Atmos. Chem. Phys. 2004 ... and on the web

- (ii) NASA-JPL Panel for Chemical Kinetics and Photochemical Data for use
in Atmospheric Studies
(Sander, Friedl, Golden, Kurylo, Huie, Orkin, Moortgat, Ravishankara,
Kolb, Molina, Finlayson-Pitts Evaluation → No 15, enduring until present)

JPL Publications on the web

(iii) Combustion data evaluations

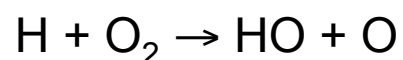
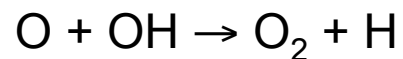
(starting as an EU task group, then under the auspices of the IUPAC Commission on Chemical Kinetics, ended in 2004;

Baulch, Bowman, Cobos, Cox, Just, Kerr, Pilling, Stocker, Troe, Tsang, Walker, Warnatz)

last publication: J. Phys. Chem. Ref. Data 34, 757 – 1397 (2005)

will never be managed again (?)

Case study



Thermochemistry: improving

Equilibrium constants: improving

Experiments: improving

Theories: potential improving
classical trajectories
quantum scattering

Intermediate HO₂

Spectroscopy: improving

Basic dilemmata unsolved: zeropoint energy in classical trajectory calculations?
low temperature experiments?
contribution of several electronic states?

analysis of the system. The value of Ingham *et al.*² is also slightly uncertain [see Comment (b)] and for present purposes their maximum value is taken. When this value is combined with the results of Eng *et al.*³ the Arrhenius function $k = 7.4 \cdot 10^{-9} \exp(-25064/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ fits the results well but the activation energy of 208 kJ mol^{-1} is considerably higher than the enthalpy of reaction, suggesting that a non-Arrhenius expression is required. Although it may be argued that the temperature exponent of 2.5 adopted in this evaluation for the reactions $\text{O}_2 + \text{RH} \rightarrow \text{HO}_2 + \text{R}$, where R is an electron-localized radical, should be enhanced by about a factor of 4 for a delocalized radical arising from decreased effects on the pre-exponential factor at high temperatures, 2.5 is maintained for consistency and the risk of

overestimating k at temperatures above those used in the study of Eng *et al.*³ the values of which are probably high by about a factor of 2.

¹J. L. Emdee, K. Brezinsky, and I. Glassman, *J. Phys. Chem.* **96**, 2151 (1992).

²T. Ingham, R. W. Walker, and R. E. Woolford, 25th Symp. (Int.) Combustion, 1994, p. 767.

³R. A. Eng, C. Fittschen, A. Gebert, P. Hibomvski, H. Hippler, and A.-N. Unterreiner, 27th Symp. (Int.) Combustion, 1998, p. 211.

⁴CEC, Supplement I, 1994 (see references in Introduction).

⁵K. Brezinsky, T. A. Litzinger, and I. Glassman, *Int. J. Chem. Kinet.* **16**, 1053 (1984).

⁶A. B. Lovell, K. Brezinsky, and I. Glassman, 22nd Symp. (Int.) Combustion, 1989, p. 1063.

⁷N. D. Stothard and R. W. Walker, *J. Chem. Soc. Faraday Trans.* **87**, 241 (1991).

H + O₂ → O + OH

Thermodynamic Data

$$\begin{aligned} \Delta H_{298}^\circ &= 68.29 \text{ kJ mol}^{-1} \\ \Delta S_{298}^\circ &= 25.04 \text{ J K}^{-1} \text{ mol}^{-1} \\ K_c &= 2.88 \cdot 10^2 T^{-0.367} \exp(-8390/T) \\ &\quad (300 \leq T/K \leq 5000) \end{aligned}$$

See Section 3 for the source of the Thermodynamic Data.

Rate Coefficient Data

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Comments |
|--|-----------|--|----------|
| <i>Rate Coefficient Measurements</i> | | | |
| $2.0 \cdot 10^{-10} \exp(-8107/T)$ | 1000–2500 | Pamdimukkala and Skinner, 1982 ¹ | (a) |
| $1.78 \cdot 10^{-10} \exp(-7400/T)$ | 1000–1350 | Vandooren, Nelson da Cruz, and Van Tiggelen, 1988 ² | (b) |
| $2.8 \cdot 10^{-10} \exp(-8118/T)$ | 962–1705 | Pirraglia <i>et al.</i> , 1989 ³ | (c) |
| $1.55 \cdot 10^{-10} \exp(-7448/T)$ | 1450–3370 | Masten, Hanson, and Bowman, 1990 ⁴ | (d) |
| $2.64 \cdot 10^{-7} T^{-0.927} \exp(-8493/T)$ | 1050–2700 | Yuan <i>et al.</i> , 1991 ⁵ | (e) |
| $1.15 \cdot 10^{-10} \exp(-6917/T)$ | 1103–2055 | Shin and Michael, 1991 ⁶ | (f) |
| $1.55 \cdot 10^{-10} \exp(-7270/T)$ | 2050–5300 | Du and Hessler, 1992 ⁷ | (g) |
| $1.38 \cdot 10^{-10} \exp(-7253/T)$ | 1336–3370 | Yu <i>et al.</i> , 1994 ⁸ | (h) |
| $1.66 \cdot 10^{-10} \exp(-7690/T)$ | 1850–3550 | Yang <i>et al.</i> , 1994 ⁹ | (i) |
| $1.18 \cdot 10^{-10} \exp(-6957/T)$ | 1050–2500 | Ryu, Hwang, and Rabinowitz, 1995 ¹⁰ | (j) |
| <i>Reviews and Evaluations</i> | | | |
| $2.77 \cdot 10^{-7} T^{-0.9} \exp(-8750/T)$ | 300–2500 | Cohen and Westberg, 1983 ¹¹ | (k) |
| $1.62 \cdot 10^{-10} \exp(-7470/T)$ | 300–2500 | CEC, 1992; 1994 ¹² | (l) |

Comments

- (a) Shock tube study on rich and stoichiometric H₂/O₂/Ar mixtures at pressures of 1.5–2.5 bar. [O] monitored by time-resolved resonance absorption.
- (b) Lean low-pressure (46 mbar) CO/H₂/O₂/Ar premixed flame. k derived from fit of O₂ reaction rate from [O₂] profiles measured by molecular beam sampling/mass spectrometry.
- (c) Shock tube study in which H atoms were produced by flash photolysis of NH₃ or H₂O in the reflected shock regime. Total pressures 13–40 mbar. [H] monitored by time-resolved resonance absorption.
- (d) Shock tube study using rich H₂/O₂/Ar mixtures at total pressures of 0.3–2.6 bar. [H] monitored by ARAS in
- incident shock experiments; absolute [OH] obtained by cw laser absorption. k derived by numerical simulations using a 23-reaction mechanism.
- (e) Shock tube study using reflected shocks in H₂/O₂/Ar mixtures at total pressures of 1.4–3.4 bar. Relative [OH] monitored by time-resolved cw laser absorption. k obtained by numerical simulations using a 19-reaction mechanism.
- (f) Shock tube study using reflected shocks in O₂/H₂O or NH₃/Ar mixtures at total pressures of 0.3–1 bar. H produced by excimer laser photolysis of H₂O or NH₃. [H] monitored by time-resolved ARAS under pseudo first order conditions.
- (g) Shock tube study using incident shocks in rich H₂/O₂/Ar mixtures at total pressures of 0.75–1.6 bar.

- [OH] determined by pulsed laser absorption. k obtained by using numerical simulations of a 17-reaction mechanism to fit the [OH] profile.
- (h) Reinterpretation of experimental data of Yuan *et al.*,⁵ and Masten *et al.*⁴
 - (i) Shock tube study using reflected shocks in rich H₂/O₂/Ar mixtures at pressures of 2.4–3.9 bar. Relative [OH] monitored by time resolved cw laser absorption. k obtained by using numerical simulations of an 11-reaction mechanism to fit the [OH] profile.
 - (j) Shock tube study using reflected shocks in rich H₂/O₂/Ar mixtures at total pressures of 0.7–4.0 bar. Relative [OH] monitored by cw laser absorption. k obtained using numerical simulations of a 20-reaction mechanism to fit the [OH] profile.
 - (k) Based on low temperature data for the reverse reaction and a number of shock tube and flame studies. Recommended expression is accepted by Tsang and Hampson.¹³
 - (l) Accepts the expression of Baulch *et al.*¹⁴ adjusted to fit data of Frank and Just¹⁵ and Pirraglia *et al.*³

Preferred Values

$$k = 3.43 \cdot 10^{-10} T^{-0.097} \exp(-7560/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the range } 800\text{--}3500 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.1 \text{ at } 800 \text{ K, rising to } \pm 0.2 \text{ at } 3500 \text{ K.}$$

Comments on Preferred Values

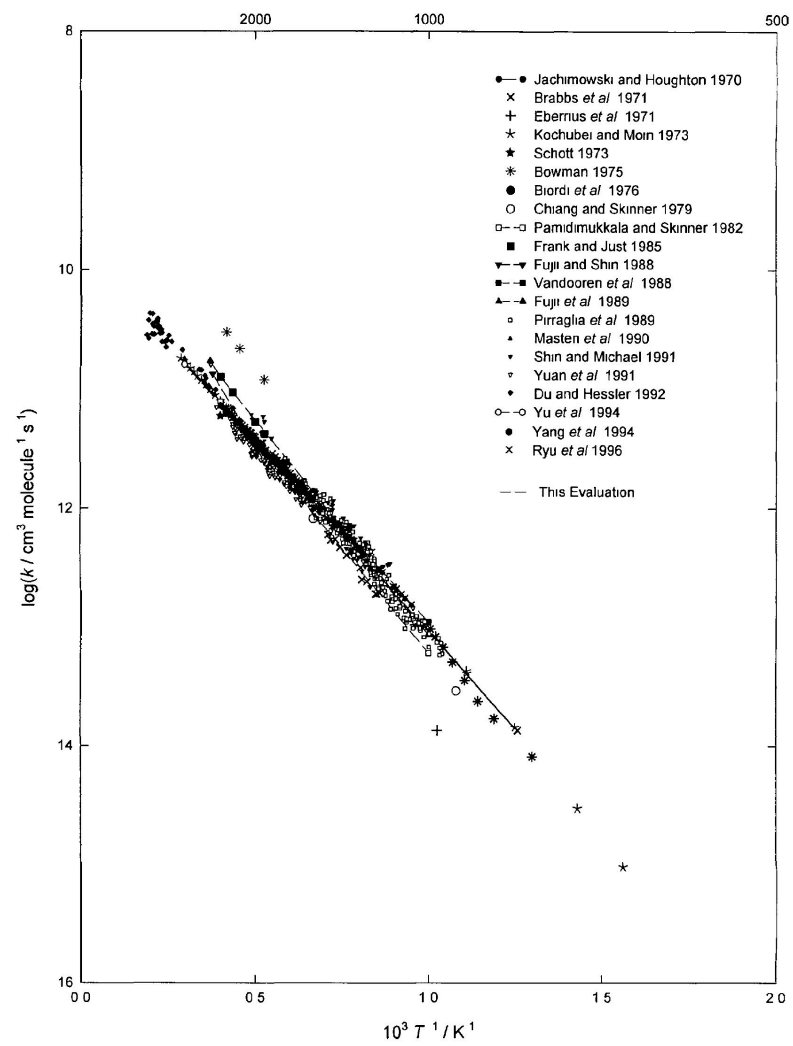
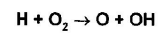
There have been numerous studies of this reaction. For clarity, only data since 1970 have been included in the Arrhenius diagram although some of the earlier data are in good agreement with those obtained more recently. The early studies have been evaluated by Baulch *et al.*¹⁴ and by Cohen and Westberg.¹¹ The review of Tsang and Hampson¹³ accepts the recommendations of Cohen and Westberg.¹¹

There are no direct measurements of k below 500 K and the recommended values are based on data obtained at temperatures above 800 K. The majority of the determinations of k have been made using shock tube techniques and, generally, are in good agreement.^{1–10,15–25} There is a trend in the

more recent studies^{1–10} to give slightly lower values of E/R than most of the older determinations.^{11,5–25} Our preferred expression for k is based on the more recent studies, which are cited in the Table. The expression derived gives values very similar to the expression used by Smith *et al.*²⁶ in modeling studies using the GRI mechanism.

References

- ¹K. M. Pamidimukkala and G. B. Skinner, Proc. 13th Int. Symp. on Shock Tubes and Waves, 1982, p. 585.
- ²J. Vandooren, F. Nelson da Cruz, and P. J. Van Tiggelen, 22nd Symp. (Int.) Combustion, 1988, p. 1587.
- ³A. N. Pirraglia, J. V. Michael, J. W. Sutherland, and R. B. Klemm, J. Phys. Chem. **93**, 282 (1989).
- ⁴D. A. Masten, R. K. Hanson, and C. T. Bowman, J. Phys. Chem. **94**, 7119 (1990).
- ⁵T. Yuan, C. Wang, C.-L. Yu, M. Frenklach, and M. J. Rabinowitz, J. Phys. Chem. **95**, 1258 (1991).
- ⁶K. S. Shin and J. V. Michael, J. Chem. Phys. **95**, 262 (1991).
- ⁷H. Du and J. P. Hessler, J. Chem. Phys. **96**, 1077 (1992).
- ⁸C.-L. Yu, M. Frenklach, D. A. Masten, R. K. Hanson, and C. T. Bowman, J. Phys. Chem. **98**, 4770 (1994).
- ⁹H. Yang, W. C. Gardiner, K. S. Shin, and N. Fujii, Chem. Phys. Lett. **231**, 449 (1994).
- ¹⁰S.-O. Ryu, S. M. Hwang, and M. J. Rabinowitz, J. Phys. Chem. **99**, 13984 (1995).
- ¹¹N. Cohen and K. R. Westberg, J. Phys. Chem. Ref. Data **12**, 531 (1983).
- ¹²CEC, 1992; Supplement I, 1994 (see references in Introduction).
- ¹³W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data **15**, 1087 (1986).
- ¹⁴D. L. Baulch, D. D. Drysdale, D. G. Horne, and A. C. Lloyd, *Evaluated Kinetic Data for High Temperature Reactions*, Vol. 1, Homogeneous Gas Phase Reactions of the H₂-O₂ System (Butterworths, London, 1972).
- ¹⁵P. Frank and Th. Just, Ber. Bunsenges. Phys. Chem. **89**, 181 (1985).
- ¹⁶K. H. Eberius, K. Hoyer, and H. Gg. Wagner, 13th Symp. (Int.) Combustion, 1971, p. 713.
- ¹⁷C. J. Jachimowski and W. M. Houghton, Combust. Flame **15**, 125 (1970).
- ¹⁸T. A. Brabbs, F. E. Belles, and R. S. Brokaw, 13th Symp. (Int.) Combustion, 1971, p. 129.
- ¹⁹V. F. Kochubei and F. B. Moin, Ukr. Khim. Zhur. **39**, 888 (1973).
- ²⁰G. L. Schott, Combust. Flame **21**, 357 (1973).
- ²¹C. T. Bowman, 15th Symp. (Int.) Combustion, 1975, p. 869.
- ²²C.-C. Chiang and G. B. Skinner, Proc. 12th Int. Symp. on Shock Tubes and Waves, 1976, p. 629.
- ²³J. C. Biordi, C. P. Lazzara, and J. F. Papp, Combust. Flame **26**, 57 (1976).
- ²⁴N. Fujii and K. S. Shin, Chem. Phys. Lett. **151**, 461 (1988).
- ²⁵N. Fujii, T. Sato, H. Miyama, F. S. Shin, and W. C. Gardiner, Proc. 17th Int. Symp. on Shock Tubes and Waves, 1989, p. 456.
- ²⁶G. P. Smith, D. M. Golden, M. Frenklach, M. Goldenber, W. C. Gardiner, V. Lissianski, C. T. Bowman, and R. K. Hanson, GRI-Mech: An Optimized Detailed Chemical Reaction Mechanism for Natural Gas Combustion, 1996.



Rate Coefficient Data

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Comments |
|--|--------------|--|----------|
| <i>Rate Coefficient Measurements</i> | | | |
| $2.0 \cdot 10^{-11} \exp(112/T)$ | 221–499 | Lewis and Watson, 1980 ¹ | (a) |
| $3.8 \cdot 10^{-11}$ | 298 | Howard and Smith, 1980 ² | (b) |
| $6.7 \cdot 10^{-10} T^{-0.5}$ | 250–515 | Howard and Smith, 1981 ³ | (b) |
| $3.1 \cdot 10^{-11}$ | 300 | Brune, Schwab, and Anderson, 1983 ⁴ | (c) |
| $3.5 \cdot 10^{-11}$ | 299 | Keyser, 1983 ⁵ | (d) |
| $4.2 \cdot 10^{-11}$ | 294 | Smith and Stewart, 1994 ⁶ | (e) |
| $4.5 \cdot 10^{-11}$ | 227 | | |
| $5.2 \cdot 10^{-11}$ | 190 | | |
| $6.1 \cdot 10^{-11}$ | 158 | | |
| <i>Reviews and Evaluations</i> | | | |
| $5.42 \cdot 10^{-13} T^{0.375} \exp(1112/T)$ | 1000–5300 | Michael, 1992 ⁷ | (f) |
| $2.0 \cdot 10^{-11} \exp(112/T)$ | 220–500 | CEC, 1992; 1994 ⁸ | (g) |
| $2.4 \cdot 10^{-11}$ | 1000–2000 | | |
| $2.2 \cdot 10^{-11} \exp(120/T)$ | 220–500 | NASA, 1997 ⁹ | (h) |
| $2.3 \cdot 10^{-11} \exp(110/T)$ | 220–500 | IUPAC, 1997 ¹⁰ | (i) |

Comments

- (a) Discharge flow system with O generated by a discharge in O₂ and OH by the H + NO₂ reaction. [OH] monitored by resonance fluorescence.
- (b) Discharge flow system with O generated by the N + NO reaction and OH by flash photolysis of H₂O. [OH] monitored by resonance fluorescence.
- (c) Discharge flow study with O atoms in excess over OH. [OH] monitored by LMR and rf, [O] by rf and absorption, and [H] by resonance fluorescence.
- (d) Discharge flow system with HO and HO₂ generated by the reaction of H with NO₂ and O₂, respectively. A steady state concentration of HO and HI₂ was established in the presence of excess O by the reaction sequence O + HO₂ → HO + O₂, O + OH → H + O₂, H + O₂ + M → HO₂ + M. [HO] monitored by rf and [HO₂] by titration with NO and detection of OH. The measured [HO]/[HO₂] gives $k/k(\text{O} + \text{HO}_2)$. Value of k calculated using $k(\text{O} + \text{HO}_2) = 5.7 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (e) Fast flow system in which OH radicals were created by pulsed laser photolysis at 266 nm of HNO₃ in the presence of a much higher concentration of O atoms previously produced upstream of the HNO₃ injection point by the N + NO reaction. [OH] was monitored by LIF, pumping at ~282.5 nm and observing at ~310 nm. The time delay between the pulse generating OH and the LIF probe pulse was varied. Results were also obtained at 103 K, 50 K, and 10 K but with large uncertainties.
- (f) Calculated from thermodynamic data and $k(\text{H} + \text{O}_2)$.
- (g) Expression of Lewis and Watson¹ adopted for low temperature range and high temperature expression derived from thermodynamic data and $k(\text{H} + \text{O}_2)$.
- (h) Based on the data of Westenberg *et al.*,¹¹ Lewis and Watson,¹ and Howard and Smith.³

- (i) Based on the data of Lewis and Watson¹ and Howard and Smith.³

Preferred Values

$k = 2.00 \cdot 10^{-10} T^{-0.352} \exp(113/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
over the range 250–3000 K.

Reliability

$\Delta \log k = \pm 0.2$ over the range 250–3000 K.

Comments on Preferred Values

The only direct studies on this reaction have been carried out at low temperatures where there is excellent agreement among the more recent of them.^{1–6} There are also a number of older studies^{11–18} where the agreement is less good but which generally support the more recent work. The data in this regime have been reviewed by the NASA⁹ and IUPAC¹¹ Panels whose findings are accepted.

Although there have been no direct measurements of k above 515 K the reverse reaction has been extensively investigated at temperatures in the range 800–3400 K. The preferred expression for k has been derived, therefore, by a fit to the data obtained by combining the expression for $k(\text{H} + \text{O}_2)$ from the present evaluation with the thermodynamic data at temperatures above 800 K together with the directly obtained experimental data at temperatures below 500 K. The reaction has been the subject of a number of theoretical studies; see Miller,^{19–21} Troe,²² Harding *et al.*,²³ and Troe and Ushakov.²⁴

¹R. S. Lewis and R. T. Watson, *J. Phys. Chem.* **84**, 3495 (1980).

²M. J. Howard and I. W. M. Smith, *Chem. Phys. Lett.* **69**, 40 (1980).

³M. J. Howard and I. W. M. Smith, *J. Chem. Soc. Faraday Trans. 2* **77**, 997 (1981).

⁴W. H. Brune, J. J. Schwab, and J. G. Anderson, *J. Phys. Chem.* **87**, 4503 (1983).

- ⁵L. F. Keyser, *J. Phys. Chem.* **87**, 837 (1983).
- ⁶I. W. M. Smith and D. W. A. Stewart, *J. Chem. Soc. Faraday Trans.* **90**, 3221 (1994).
- ⁷J. V. Michael, *Prog. Energy Combust. Sci.* **8**, 327 (1992).
- ⁸CEC, 1992; Supplement I, 1994 (see references in Introduction).
- ⁹NASA Evaluation No. 12, 1997 (see references in Introduction).
- ¹⁰IUPAC, Supplement VI, 1997 (see references in Introduction).
- ¹¹A. A. Westenberg, N. de Haas, and J. M. Roscoe, *J. Phys. Chem.* **74**, 3431 (1970).
- ¹²I. M. Campbell and B. J. Handy, *Chem. Phys. Lett.* **47**, 475 (1977).
- ¹³J. E. Breen and G. P. Glass, *J. Phys. Chem.* **52**, 1082 (1970).
- ¹⁴A. A. Westenberg and N. de Haas, *J. Chem. Phys.* **43**, 1550 (1965).
- ¹⁵F. Kaufman, *Ann. Geophys.* **20**, 106 (1964).
- ¹⁶F. Kaufman and F. P. Del Greco, *Proceedings 9th Symposium (Int.) Combustion*, 1963, p. 211.
- ¹⁷F. P. Del Greco and F. Kaufman, *Discuss Faraday Soc.* **33**, 128 (1962).
- ¹⁸M. A. A. Clyne, *9th Proceedings Symposium (Int.) Combustion*, 1963, p. 211.
- ¹⁹J. A. Miller, *J. Chem. Phys.* **84**, 6170 (1986).
- ²⁰J. A. Miller, *Proceedings 26th Symposium (Int.) Combustion*, 1996, p. 461.
- ²¹T. C. Germann and W. H. Miller, *J. Phys. Chem. A* **101**, 6358 (1997).
- ²²J. Troe, *Proceedings 22nd Symposium (Int.) Combustion*, 1988, p. 843.
- ²³L. B. Harding, A. I. Maergoiz, J. Troe, and V. G. Ushakov, *J. Chem. Phys.* **113**, 11019 (2000).
- ²⁴J. Troe and V. G. Ushakov, *J. Chem. Phys.* **115**, 3621 (2001).

